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**APPROACHES TO LADDER STRUCTURES VII.  
POLYCONDENSATION OF AROMATIC DIAMINO  
DICARBOXYLIC ACIDS WITH DIMETHYLFORMAMIDE  
AND PHOSPHORUS PENTOXIDE**

*GERARD A. LOUGHRAN*

TECHNICAL REPORT AFML-TR-71-87

FEBRUARY 1972

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. G. A. Loughran as Project Scientist.

This report covers work conducted from October 1967 to January 1970. The manuscript was released by the author in July 1970 for publication as a technical report.

The author wishes to thank Dr. G. F. L. Ehlers of the Polymer Branch (LNP), Air Force Materials Laboratory, for the TGA curves; Mr. Lee Smithson, and other personnel of the Analytical Branch (LPA), Air Force Materials Laboratory for the Mass Spectral Data, Microanalyses, and VPO Molecular Weight Determinations; Miss Mary Ryan for the Nuclear Magnetic Resonance Spectra, and Mr. Jerald L. Burkett of the University of Dayton Research Institute for the viscosity determinations.

This technical report has been reviewed and is approved.



R. L. VAN DEUSEN  
Chief, Polymer Branch  
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## ABSTRACT

It has been found that a new compound, 6-dimethylamino-carbonyl-dibenzo-[b,f] [1,5]-diazocine-12, [11H]-one, is produced when either anthranilic acid or dibenzo-[b,f] [1,5]-diazocine-6,12, [5H,11H]-dione is heated at 50 to 80° C in solution in dimethylformamide in the presence of a suspension of phosphorus pentoxide. A mechanism involving self condensation of anthranilic acid to dibenzo-[b,f] [1,5]-diazocine-6,12, [5H,11H]-dione followed by reaction with dimethylformamide is proposed.

Polycondensation of ortho substituted diamino aromatic dicarboxylic acids such as 2,5-diaminoterephthalic acid, or benzidine-3,3'-dicarboxylic acid occurs in a similar fashion resulting in formation of double strand or ladder polymers of high molecular weight which can be extruded into fibers from concentrated sulfuric acid or from methane sulfonic acid. These new ladder polymers have a high degree of thermal stability and contain at least one dimethylaminocarbonyl group for each unit in the polymer chain. The polymers appear to be hydroscopic and easily absorb water to give a hydrated structure which contains about one molecule of water for each dimethylaminocarbonyl group. This absorbed water is removable by vacuum drying.

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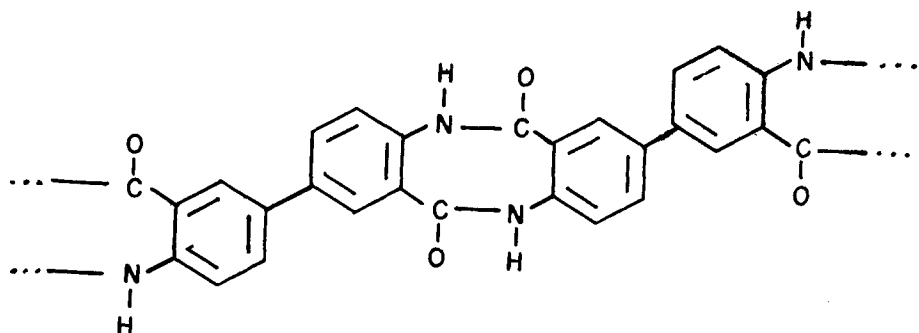
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# SECTION I

## INTRODUCTION

This work is concerned with the preparation of soluble high molecular weight double strand polymers related to poly-(5,6,11,12-tetrahydro-6,12-dioxodibenzo-[b,f] [1,5]-diazocine-2,8 diyl), X, Such double strand polymers can be expected to exhibit a high degree of thermal stability.



Recently, Kurihara and Yoda studied the condensation of ortho amino dicarboxylic acids, and certain ortho substituted diamino dicarboxylic acids in polyphosphoric acid (References 1 and 2). For instance, they observed that condensation of anthranilic acid, I, in polyphosphoric acid did not result in the formation of the desired model compound, dibenzo-[b,f] [1,5]-diazocine-6,12, [5H, 11H]-dione, III. Instead a 59% yield of 2-(o-aminophenyl)-[4H],3,1-benzoxazine-4-one, VII, was obtained. They synthesized the model compound, III, by another method (Reference 7) and studied its behavior in polyphosphoric acid. After heating III at 150 to 160°C in polyphosphoric acid for a short time, about 25% of the starting material had apparently rearranged to VII. When the temperature was raised to 240°C, a compound of higher molecular weight,  $C_{28}H_{16}O_2N_4$  was obtained. This was not further characterized by Kurihara and Yoda.

They found that the polycondensation of such aromatic diamino dicarboxylic acids as 2,5-diaminoterephthalic acid, VIII, benzidine-3,3'-dicarboxylic acid, XIII, or methylenedianthranilic acid, in polyphosphoric acid at 150 to 160°C gave only linear single strand polyamides with pendant amino and carboxylic acid groups. Later work by Loughran (Reference 5) confirms that a desired double stranded polymer, X, or XV, is not readily obtained by this method.

It became of interest therefore to find whether a convenient method could be found to bring about polycondensation of aromatic diaminodicarboxylic acids accompanied by or followed by ring closure under relatively mild conditions to give soluble high molecular weight double strand polymers related to poly-(5,6,11,12-tetrahydro-6,12-dioxodibenzo-[b,f]-[1,5]-diazocine-2,8-diyl), XV. Since phosphorus pentoxide,  $P_2O_5$ ,\* is known to dissolve in hot dimethylformamide, it was thought that such a solution, or even a suspension of it, in dimethylformamide might be a useful reagent for polycondensation and ladder polymer formation.

\* The molecular formula for phosphorus pentoxide is actually  $P_4O_{10}$  based on molecular weight measurements and structural studies.

## SECTION II

### DISCUSSION OF RESULTS

#### A. Model Compounds and Model Reactions

In order to determine whether the solvent, in this case dimethylformamide, takes part in the polycondensation, a model reaction involving the condensation of anthranilic acid, I, in dimethylformamide with phosphorus pentoxide, was studied. Anthranilic acid, I, was dissolved in dimethylformamide stirred with a suspension of phosphorus pentoxide at 60 to 80°C. The sole product isolated from the reaction mixture crystallized from ligroin as white needles, mp 137°C. Analytical results indicate that its molecular formula lies close to  $C_{17}H_{15}O_2N_3$ , and its molecular weight was found to be 310 by the VPO method in benzene (Theory 293).

Its infrared spectrum (run in KBr) exhibits a weak sharp band near  $3030\text{ cm}^{-1}$  attributed to the aromatic-CH stretching vibration, while weak absorption observed near  $2950\text{ cm}^{-1}$  is probably due to aliphatic-C-H stretching vibrations. The strong band at  $1670\text{ cm}^{-1}$  appears to be due to amide I carbonyl absorption. The infrared spectrum of the compound (in KBr) is shown in Figure 4 while the solution spectrum (in  $CCl_4$ ) is shown in Figure 5.

The molecular ion peak appears in its mass spectrum (Figure 6) at m/e 293. The number of carbon atoms in the molecule was calculated from the intensity of the lines at m/e 293 and m/e 294, and from the  $^{13}C/^{14}C$  ratio, and found to be 17. This data along with the analytical results and molecular weight determination confirms the molecular formula of the compound as  $C_{17}H_{15}ON_2$ . Two structural formulas, IV, (Figure 1) are possible.

A nuclear magnetic resonance spectrum (Figure 7) run in  $CDCl_3$  at room temperature indicates that a ratio of aromatic protons near 8 ppm to aliphatic protons at 3 ppm is of the order of 1.5 to 1.0. This is close to the ratio expected based on 8 protons (4 each) attached to the aromatic

rings and one amide proton which likely appears in this region. Thus six aliphatic protons in the form of two methyl groups can be expected. These aliphatic protons appearing as a doublet at 3 ppm appear to be non-equivalent, as in dimethylformamide. When the spectrum was run in  $\text{CDCl}_3$  at  $50^\circ\text{C}$ , the doublet disappeared, indicating that the protons on the methyl groups had become equivalent on heating (Figure 8).

In order to determine which of the two structures, IV or VI (Figure 1) can be assigned to the reaction product, mp  $137^\circ\text{C}$ , from anthranilic acid, I, dimethylformamide, and phosphorus pentoxide, the reaction of dibenzo-[b,f]-diazocine-6,12,[5H, 11H]-dione, III with dimethylformamide and phosphorus pentoxide was considered. One might suspect that anthranilic acid, I, and /or its initial condensation product, N-( $\bar{o}$ -aminobenzoyl)anthranilic acid, II, could react with dimethylformamide to give the corresponding Shiff base or amidine, V, since it is known that amino-anthraquinones react with dimethylformamide in the presence of acidic dehydrating agents such as thionyl chloride (Reference 15). Then subsequent dehydration of the Shiff Base, V, might result in formation of 6-dimethylamino-dibenzo-[b,f] [1,5]-diazonine-7,13, [12H]-dione, VI. On the other hand the self condensation of anthranilic acid, I, through N-( $\bar{o}$ -aminobenzoyl)-anthranilic acid, II, to dibenzo-[b,f] [1,5]-diazocine-6,12,[5H, 11H]-dione, III, also can be expected and tautomerization of III followed by reaction with dimethylformamide could lead to the formation of 6-dimethylaminoformyl-dibenzo-[b,f] [1,5]-diazocine-12, [11H]-one, IV (Figure 1).

Hence, dibenzo-[b,f] [1,5]-diazocine-6,12,[5H, 11H]-dione, III, was dissolved in dimethylformamide, and the solution was stirred with powdered phosphorus pentoxide at room temperature for four hours. Subsequently the reaction mixture was heated at  $50$  to  $90^\circ$  over 18 hours. The reaction product after recrystallization from ligroin as white needles, mp  $137^\circ\text{C}$ . Its infrared spectrum (Figure 9) is identical with that from the reaction product of anthranilic acid, I, dimethylformamide, and phosphorus pentoxide. Hence structure V is ruled out, and the reaction product of anthranilic

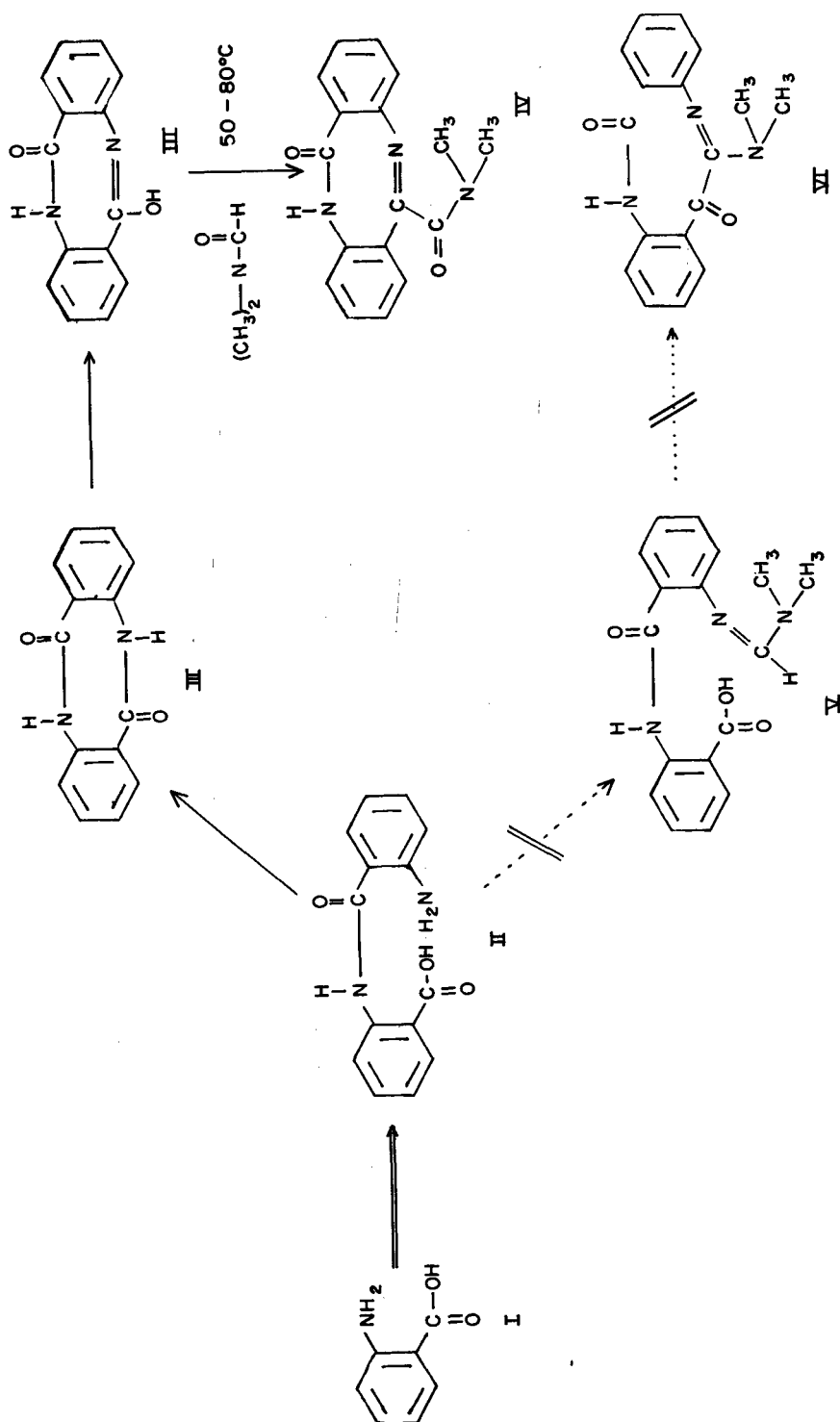


Figure 1 Reaction of Anthranilic Acid, I, and Dibenzo-[b,f] [1,5]-diazocine-6,12-[5H, 11H]-dione III with Dimethylformamide and Phosphorus Pentoxide.



acid, I, dimethylformamide and phosphorus pentoxide is identified as 6-dimethylaminocarbonyl-dibenzo-[b,f] [1,5]-diazocine-12, [11H]-one, IV. The equations for its formation appear in Figure 1.

## B. Polymerization Reactions

### 1. Polycondensation of 2,5-diaminoterephthalic acid, VIII, with Dimethylformamide and Phosphorus Pentoxide.

Obviously then, based on the results of the model reaction, it can be predicted that dimethylformamide would likely take part in a polycondensation reaction involving an aromatic diaminodicarboxylic acid. The course of such a polycondensation under mild conditions of low temperature and low concentration of phosphorus pentoxide may result in the initial formation of a linear polyamide with pendant amino and carboxylic acid groups. Subsequently, this prepolymer, under the more vigorous conditions of higher temperature, longer reaction time, and higher concentration of phosphorus pentoxide may be converted by ring closure into a ladder polymer containing [b,f] [1,5]-diazocine-6, 12, [5H, 11H]-dione units: Reaction of dimethylformamide with this polymer then can be expected to result in formation of a ladder polymer with pendant dimethylaminocarbonyl groups attached to the polymer chain. The extent of such a side reaction on the polymer can be expected to vary with conditions.

The polycondensation of 2,5-diaminoterephthalic acid, VIII, in dimethylformamide in the presence of phosphorus pentoxide was studied with some variation in conditions. Initially the polymerization reaction was carried out by stirring the finely divided monomer with a solution of phosphorous pentoxide in dimethylformamide under a nitrogen atmosphere. When temperatures as high as 120°C (Run A) were employed, the polymer was of low molecular weight having an inherent viscosity ( $\eta_{inh}=0.14$ ). Its TGA curve is shown in Figure 10. It had a limited solubility in concentrated sulfuric acid, and was insoluble in dimethylformamide. When a maximum reaction temperature of 100°C was employed (Run B), a mixture of two polymers was obtained. One was soluble in concentrated

sulfuric acid, and in dimethylformamide and had a molecular weight of 4920. The other was insoluble in dimethylformamide, and had an inherent viscosity, of 0.26. A higher molecular weight material was obtained when a solution of 2,5-diaminoterephthalic acid disulfate was stirred with a suspension of phosphorus pentoxide at 60°C (Run C). The resulting polymer was soluble both in dimethylformamide and in concentrated sulfuric acid or methane sulfonic acid. Its inherent viscosity (in methane sulfonic acid) was in the 0.54 to 0.58 range with molecular weight values near 6600.

In all these runs the monomer concentration in moles per liter of dimethylformamide varied from 0.023 to 0.066 while the ratio of phosphorous pentoxide to moles of monomer varied from 8.7 to 18.9. Analytical results indicate that the polymer from Run B has a molecular formula approaching  $(C_{22}H_{22}O_6N_6)_n$  indicating it probably has the hydrated structure, XII, (Figure 2). The polymer from Run C, after drying at 180°C/0.1 mm appears to have a molecular formula  $(C_{22}H_{18}O_4N_6)$ , XI, (Figure 2).

A typical infrared spectrum of the polymer  $(C_{22}H_{22}O_6N_6)_n$ , represented by structure XII, obtained from Run B, is illustrated in Figure 11. A strong water band is evident near  $3500\text{ cm}^{-1}$ . The presence of a sharp weak band near  $3030\text{ cm}^{-1}$  is apparently due to the aromatic stretching vibration while absorption in the  $2950\text{ cm}^{-1}$  region is attributed to aliphatic -CH stretching vibrations, suggesting that reaction with dimethyl formamide has taken place. The absence of two strong bands near  $3300\text{ cm}^{-1}$  as well as the absence of broad absorption due to bonded -OH stretching vibrations in the  $2500\text{ cm}^{-1}$  to  $2700\text{ cm}^{-1}$  region indicates that no unreacted -NH<sub>2</sub> groups, or -COOH groups are present. Obviously the polymers are not single strand linear polymers with pendant amino and carboxylic acid groups, and it appears likely that they possess ladder structures related to the dibenzo-[b,f] [1,5]-diazocine moiety. It also seems evident that dimethylformamide has reacted with the polymer, probably in a manner similar to the reaction of anthranilic acid, I, dimethylformamide and phosphorous pentoxide described above. It is interesting to note that the strong OH band at  $3500\text{ cm}^{-1}$  disappears when the KBr "window" (Reference 21) is dried in a vacuum pistol at 100 to 180°C/0.05

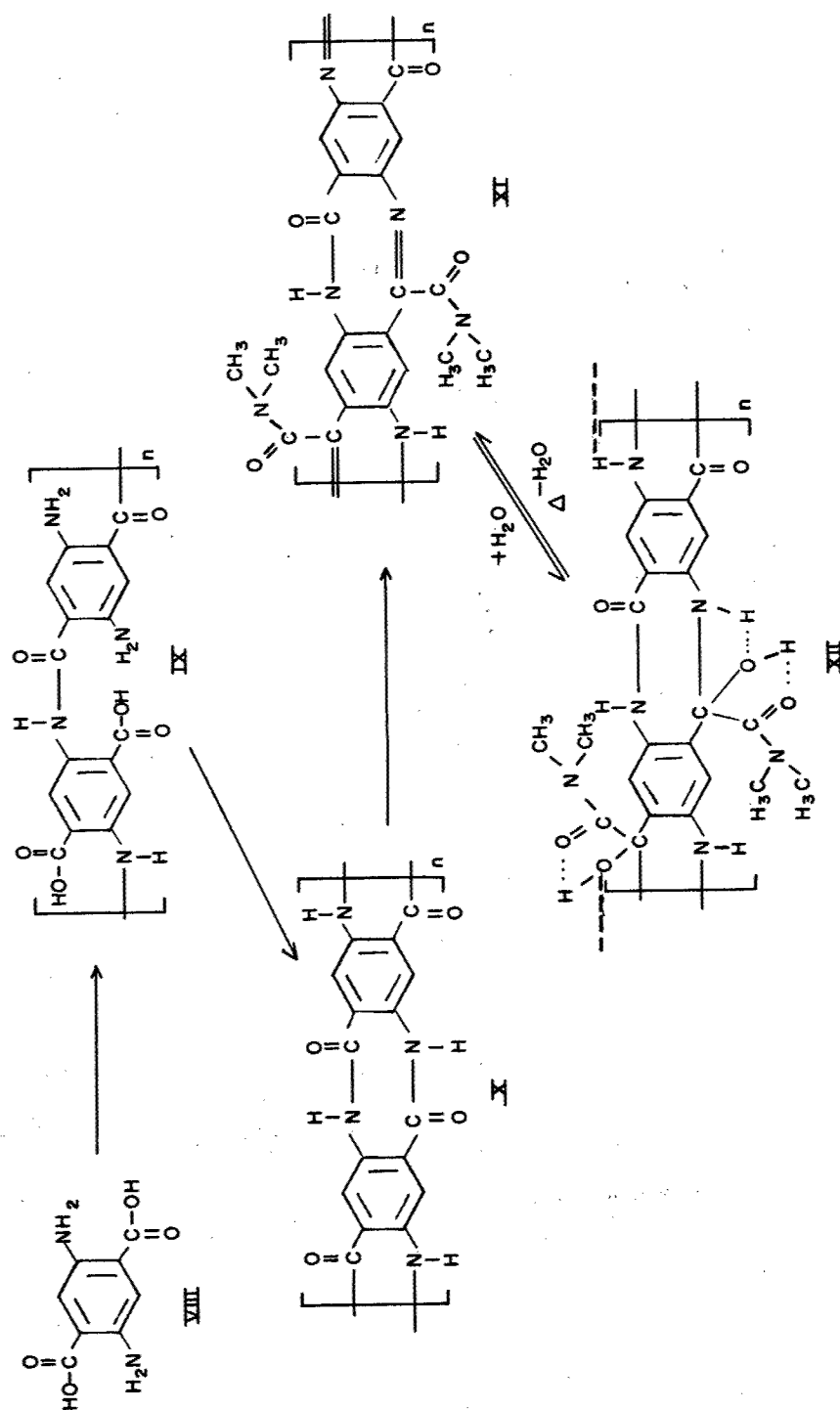


Figure 2 Polycondensation of 2,5-diaminoterephthalic acid, VIII with Dimethylformamide and Phosphorus Pentoxide

mm for a suitable time. The band reappears when the KBr "window" is exposed to the air, indicating that the polymer is hygroscopic. The polymer from Run B appears to have a calculated molecular formula  $(C_{22}H_{22}O_6N_6)_n$  indicating that it too is probably a hydrated structure represented by XII in Figure 2. When the polymer, XI, (from Run C) was heated at 300°C/0.03 mm for 24 hours an insoluble material was obtained. Analytical results suggest that some degradation may have taken place since the values for % C and % N are much lower (Table IV).

The polymer from Run A is obviously an impure version of the hydrated product  $(C_{22}H_{22}O_6N_6)_n$ , XII. It does contain an appreciable quantity of phosphorus. Its thermal stability characteristics are fair. Under TGA conditions about 53% weight residue remains at 900°C. Degradation appears to progress slowly at a steady rate apparently beginning somewhere between 200 and 300°C. Its TGA curve is shown in Figure 10.

A comparison of the results of the preparations are given in the Tables 1, 3, and 4. The structures, XI and XII, are shown along with the equation for their preparation in Figure 2. Thus, at relatively low temperatures 2,5-diaminoterephthalic acid, VIII, or its disulfate probably undergo initial self condensation to give a linear single strand polymer,  $(C_{16}H_{12}O_8N_4)_n$ , IX, which then undergoes cyclodehydration to the double stranded structure,  $(C_{16}H_8O_4N_4)_n$ , known as Poly-[5,6,11,12-tetrahydro-6,12-dioxodibenzo-[b,f] [1,5]-diazocine-2,3,8,9-tetrayl-2,8-dimino-3,9-dicarbonyl, X. Subsequently, tautomerization followed by a dehydration reaction with dimethylformamide occurs to give the new polymer  $(C_{22}H_{18}O_4N_6)_n$ , XI, which readily hydrates to give  $(C_{22}H_{22}O_6N_6)_n$ , XII.

2. Polycondensation of Benzidine - 3,3'-dicarboxylic acid, XIII, with Dimethylformamide, and Phosphorus Pentoxide.

In order to obtain polymers of higher molecular weight, the self condensation of benzidine-3,3'-dicarboxylic acid, VI, in dimethylformamide in the presence of phosphorus pentoxide was run under a variety of conditions. First the condensation polymerization was carried out in a

TABLE I

VARIATION OF MOLECULAR WEIGHT WITH THE MOLAR CONCENTRATION OF MONOMER  
IN DIMETHYLFORMAMIDE AND WITH THE PHOSPHOROUS PENTOXIDE - MONOMER  
RATIO IN THE POLYCONDENSATION OF 2,5-DIAMINOTEREPHTHALIC ACID,  
VII, WITH DIMETHYLFORMAMIDE AND PHOSPHORUS PENTOXIDE

Run No.	Moles P <sub>4</sub> O <sub>10</sub>		Monomer Conc. Moles/Liter DMF	Reaction Temperature °C	Viscosity η <sub>inh</sub>	Structure
	Moles Monomer					
A	18.9		0.023	100 -120	0.14	XII
B	8.7		0.066	90 -100	0.26	XII
C	13.9		0.033	60	0.58	XI

solution of phosphorous pentoxide in dimethylformamide in a nitrogen atmosphere. One disadvantage of this method is that the reagent dissolves very slowly in the solvent. It was usually necessary to stir the reaction mixture vigorously at 100 to 120° for 24 hours or longer to dissolve all the solid phosphorous pentoxide. Eventually, the reaction mixture became a dark reddish-brown liquid. The benzidine-3,3'-dicarboxylic acid, XIII, was added to this solution in some cases as a solid; otherwise a solution of XIII in dimethylformamide was added dropwise, and the reaction mixture was stirred at the temperature and time indicated in Table V. When temperature ranges of 90 to 120°C were employed, the polymeric products obtained were insoluble both in dimethylformamide and in concentrated sulfuric acid regardless of the molar ratios of monomer to solvent, or of phosphorous pentoxide to monomer. In two runs (A and B) the reaction was carried out at 70 to 100°C with a monomer-solvent ratio at 0.05 mole/liter. When a 2.3 molar ratio of phosphorous pentoxide to monomer was used (Run A), a low molecular weight polymer,  $(C_{17}H_{15}O_3N_3)_n$ , XVII, was obtained. Its molecular weight was found to be 950 (measured by the VPO method in dimethylformamide). The polymer was soluble in dimethylformamide, in concentrated sulfuric acid, and in methane sulfonic acid. When a molar ratio of phosphorous pentoxide to monomer was increased to 11.7 (Run B), higher molecular weight polymers were obtained. About 28% of the reaction product was soluble in dimethylformamide and had a molecular weight of 4375 (measured by the VPO method in dimethylformamide). The remainder of the product, 62%, was soluble in concentrated sulfuric acid. Its inherent viscosity, was 0.4. Repetition of this reaction at 80°C (Run H) with a molar ratio of phosphorous pentoxide to monomer of 23.0 and with a reduction in monomer concentration to about 0.02 moles per liter, gave a polymer with an inherent viscosity, of 0.36. When the reaction temperature was kept as high as 120°C, insoluble polymers,  $(C_{17}H_{15}O_3N_3)_n$ , were obtained (Runs C and D).

The reaction conditions were modified so that a solution of the monomer in dimethylformamide was treated at 30 to 50°C with a suspension of powdered phosphorous pentoxide and the reaction mixture was stirred at the temperature range indicated in Table V. Best results were obtained

when the reaction temperature was kept at 50 to 80°C for the bulk of the reaction time (133 to 168 hours), being allowed to rise to 90°C towards the end of the reaction period. When the monomer/solvent ratio was kept at 0.34 moles/liter (Runs E, F and G), and the phosphorous pentoxide - monomer molar ratio varied from 14.1 to 25.2, high molecular weight polymers,  $(C_{17}H_{15}O_3N_3)_n$ , XVII, with inherent viscosities, varying from 1.44 to 2.35 were obtained.

In each of these runs a small amount of low molecular weight polymer soluble in dimethylformamide was obtained. This was isolated from the reaction mixture by decanting the solution consisting of low molecular weight polymer and dissolved phosphorous pentoxide in dimethylformamide from the insoluble resin consisting of a complex of high molecular weight polymer and phosphorous pentoxide. Treatment of the solution with benzene resulted in precipitation of the low molecular weight polymer as a translucent tacky material. The products were isolated after treatment with methanol or water. Inherent viscosities, as low as 0.18 and as high as 0.57 were obtained.

The high molecular weight polymer (complexed with phosphorous pentoxide) had precipitated from and was insoluble in the reaction mixture. It was isolated by washing with benzene and stirring into cold water or methanol. These high molecular weight polymers from runs E, F, and G were more easily soluble in methane sulfonic acid than in concentrated sulfuric acid. The high molecular weight double strand polymers from runs E, F, and G exhibit good thermal stability characteristics retaining 64 to 68% weight residue at 900°. Their TGA curves are shown in Figures 15 and 16.

When the monomer/solvent ratio was increased to 0.06 moles per liter of dimethylformamide and the molar ratio of phosphorous pentoxide to monomer was increased to 36.8 (Run I), a low molecular weight polymer  $(C_{17}H_{15}O_3N_3)_n$ , XVII with an inherent viscosity, of 0.15 was obtained. Its TGA curve is illustrated in Figure 17. A further increase in the monomer/solvent ratio to 0.2 moles/liter of dimethylformamide, and in the molar ratio of phosphorous pentoxide to monomer up to 42, (Run J),

TABLE II

VARIATION OF MOLECULAR WEIGHT WITH THE MOLAR CONCENTRATION  
OF MONOMER IN DIMETHYLFORMAMIDE AND WITH THE PHOSPHOROUS  
PENTOXIDE - MONOMER RATIO IN THE CONDENSATION POLYMERIZATION  
OF BENZIDINE-3,3'-DICARBOXYLIC ACID, XIII, WITH  
DIMETHYLFORMAMIDE AND PHOSPHORUS PENTOXIDE

Run	Moles $P_4O_{10}$	Monomer Conc.	Reaction	Viscosity	Structure
No.	Moles Monomer	Moles/Liter DMF	Temperature °C	$\eta_{inh}$	
[A]	2.3	0.050	70 -120	926-950 <sup>+</sup>	XVII
[B]	11.7	0.050	90	0.40	XVII
[C]	17.6	0.075	90 -120	insol.	XVII
[D]	23.6	0.050	100 -120	-	XVII
[E]	14.1	0.033	60	1.44	XVII
[F]	14.1	0.033	50 -80	2.35	XVII
[G]	25.2	0.033	60 -90	1.70	XVII
[H]	23.0	0.019	80	0.36	XVII
[I]	36.8	0.060	60 -80	0.15	XVII
[J]	42.0	0.200	60 -90	0.14	XV
[K]	35.2	0.100*	150	insol.	XVII

\* In a mixture of dimethylformamide and dioxane.

+ Molecular weight by the VPO method in dimethylformamide.



led to formation of a low molecular weight polymer with an inherent viscosity, of 0.14. On the basis of analytical results the polymer appears to have an empirical formula approaching  $(C_{14}H_{10}O_3N_2)_n$ . This suggests that it is probably a linear polyamide containing pendant amino and carboxylic acid groups. Such a structure, is depicted by structure XIV in Figure 3. The structure is confirmed by its infrared spectrum (Figure 18) which closely resembles that obtained from a polymer  $(C_{14}H_{10}O_3N_2)_n$ , XIV, which had previously been prepared by reaction of 6,6'-bis ([2H],3,1-benzoxazine-2,4[1H]-dione) and benzidine-3,3'-dicarboxylic acid, XIII (Reference 3). This infrared spectrum is shown in Figure 21.

It almost appears as if a high molar ratio of phosphorous pentoxide to monomer and/or a high molar concentration of monomer in dimethylformamide favors formation of a linear polyamide with pendant amino and carboxylic acid groups. However, when a molar ratio of phosphorous pentoxide to monomer of 35.2 and a monomer concentration of 0.1 mole per liter of dimethylformamide was employed, and the reaction temperature was raised to 150°C, (Run K) an insoluble polymer was obtained. The product contains some phosphorus, and analytical results are poor. However, correlation with the infrared spectral data (Figure 19) suggests that the product is a cross-linked version of the ladder structure,  $(C_{17}H_{15}O_3N_3)_n$ , XVII. Its TGA curve is shown in Figure 20.

The polymers usually were difficult to purify. In some cases it was especially difficult to remove all of the phosphorus. Where appreciable amounts of phosphorus were present, high percent ash values were encountered. Washing of the polymer in dilute aqueous sodium bicarbonate followed by washes with dilute acetic acid or water usually gave products with appreciable ash. The use of dilute ammonium hydroxide instead gave better results. The most effective way to remove the phosphorus remained to dissolve the polymer in methane sulfonic acid, and recover the product as a high molecular weight material by precipitation into methanol. After Soxhlet extraction with methanol the products were vacuum dried from 100°C/0.1 mm up to 180°C/0.05 mm. It was difficult to completely dry the

polymers because they appeared to be water sensitive. This is demonstrated by comparing the infrared spectra from the KBr "windows" before and immediately after vacuum drying at 100 to 180°C/0.05 mm.

In particular this can be illustrated by a comparison of the infrared spectra from the polymer  $(C_{17}H_{15}O_3N_3)_n$ , XVII, ( $\eta_{inh} = 2.35$ ), obtained from KBr "windows" (Reference 21) before and after vacuum drying at 180°C/0.01 mm (Figures 13 and 14). The strong band appearing at  $2500\text{ cm}^{-1}$ , due to the presence of water, disappears completely on vacuum drying, giving XVII, but reappears if the KBr "window" is allowed to stand long enough in the air.

Two bands appear in the spectra, one near  $3030\text{ cm}^{-1}$  is due to an aromatic -CH stretching vibration, while the other near  $2950\text{ cm}^{-1}$  can be attributed to an aliphatic -CH stretching vibration from the methyl groups. This suggests that dimethylformamide has reacted. The absence of two sharp bands in the  $3300\text{ cm}^{-1}$  region indicates that no unreacted  $NH_2$  groups are present. Such bands always appear in the spectra of aromatic polyamides (Figure 21) containing pendant amino groups. The absence of broad absorption in the  $2500\text{ cm}^{-1}$  to  $2100\text{ cm}^{-1}$  region indicates that pendant carboxylic acid groups are missing. The very strong band appearing near  $1680\text{ cm}^{-1}$  is probably due to amide I carbonyl absorption. Therefore, evidence appears to indicate that the polymers XVI and XVII have a double stranded structure and that dimethylaminoformyl groups are present. These observations parallel those obtained from the infrared spectra of the polymers XI and XII from 2,5 diaminoterephthalic acid, VIII, dimethylformamide and phosphorous pentoxide, and indicate that certain similarities exist.

Analytical results obtained from all of the initial polymer samples (except in Run J) indicate that the empirical formula is close to  $(C_{17}H_{15}O_3N_3)_n$ , XVII for which the calculated values for the elements are: % C, 66.10; % H, 4.80; and % N, 13.60. However, the elemental analyses do not agree with those predicted for the ladder polymer, poly-(5,6,11,12-

tetrahydro-6,12-dioxodibenzo-[b,f] [1,5]-diazocine-2,8-diyl),  $(C_{14}H_8O_2N_2)_n$ , XV, where the calculated values for the elements are: % C, 71.18, % H, 3.41, % N, 11.86.

A correlation the analytical results with infrared spectral data suggests that dimethylformamide has reacted with the polymer. Therefore, a structure  $(C_{17}H_{13}O_2N_3)_n$ , XVI, similar to that obtained from the condensation of anthranilic acid with dimethylformamide and phosphorous pentoxide, VI, or its hydrated counterpart,  $(C_{17}H_{15}O_3N_3)_n$ , XVII, was expected. Obviously, the initial polymeric product isolated appears to be the hydrated polymer, poly-(6-hydroxy-6-dimethylaminocarbonyl-5,6,11,12-tetrahydro-12-oxodibenzo-[b,f] [1,5]-diazocine-2,8-diyl), XVII.

Isolation of a pure sample of the anhydrous polymer, poly-(6-dimethylaminocarbonyl-11,12-dihydro-12-oxo-dibenzo-[b,f] [1,5]-diazocine-2,8-diyl),  $(C_{17}H_{13}O_2N_3)_n$ , XVI, proved to be difficult because the polymer appears to be extremely hygroscopic. This has been demonstrated by the disappearance of the strong -OH band from the infrared spectrum of the hydrated polymer, XVII, on vacuum drying, and by its rapid reappearance on standing in air. Several samples of the polymer, XVII, were dried in a vacuum pistol at temperatures ranging from 100 to 180°C and at pressures varying from 0.01 mm to 0.1 mm for periods ranging from three hours to as long as three weeks. After drying the samples were stored in a vial fitted with a plastic cap containing a polyethylene liner and sent for analysis. Sometimes as long as three to four weeks would pass before results were obtained, and they appeared to indicate that dehydration of XVII was unsuccessful. However, when a sample of the high molecular weight polymer, inherent viscosity 2.35, XVII was dried at 180°C/0.01 mm for periods from 24 to 72 hours, and the analytical samples were immediately weighed by the analyst under anhydrous conditions (in a dry box), results indicated that substantial dehydration of XVII to XVI had taken place. Complete dehydration apparently was not achieved, although the values for elemental analyses of % C, 68.61, % H, 4.48, % N, 13.92; approach the theoretical values of % C, 70.10, % H, 4.80, % N, 14.42 quite closely.

An equation illustrating the formation of the polymers and a comparison of the structures of the ladder polymer, XVI, and its hydrated counterpart, XVII, appear in Figure 3.

### C. Polymer Properties

The fiber forming capability of the high molecular weight polymer samples were investigated. When a 4% solution of the hydrated polymer, XVII, inherent viscosity 2.35, in methane sulfonic acid was forced from a syringe into water, small short fibers were produced. In order to check out the fiber forming capability of the anhydrous polymer, XVI, a sample of the hydrated polymer, XVII, inherent viscosity 1.7, was first vacuum dried at 180°C/0.01 mm for 72 hours. The dried polymer XVII, was stirred at room temperature with sufficient methane sulfonic acid to make a solution of 6.9% concentration. After two days of stirring some undissolved "gel like" material remained undissolved. The concentration of the solution was reduced to 5% and transferred by Mr. Walter Gloor, AFML/LNF, to a syringe and filtered through stainless steel mesh plates into another syringe. This syringe was kept at 60 to 80°C for 11 days, and extrusion into water gave short lengths of fiber. The remainder of the solution was heated for two more days. A spinarett trial at this point gave no fibers. The solution had decreased in viscosity over this long period of time apparently as a result of chain scission due to hydrolysis of the polymer under acid conditions at elevated temperatures.

Chain scission was further demonstrated when a solution of the hydrated polymer, XVII,  $\eta_{inh} = 1.40$  at a 5% concentration in methane sulfonic acid was heated at 50°C for 72 hours in a closed flask. This resulted in a decrease in inherent viscosity to 0.94. These results certainly indicate that the hydrated polymer, XVII, is sensitive to hydrolysis under acid conditions under moderate heating. It also appears that some crosslinking may have taken place when an attempt was made to convert the hydrated polymer, XVII, to the anhydrous polymer, XVI, by heating at 180°C/0.01 mm, because the sample was difficult to dissolve and apparently contained some gelled material. This temperature may have been too high, and as a result a small amount of the insoluble

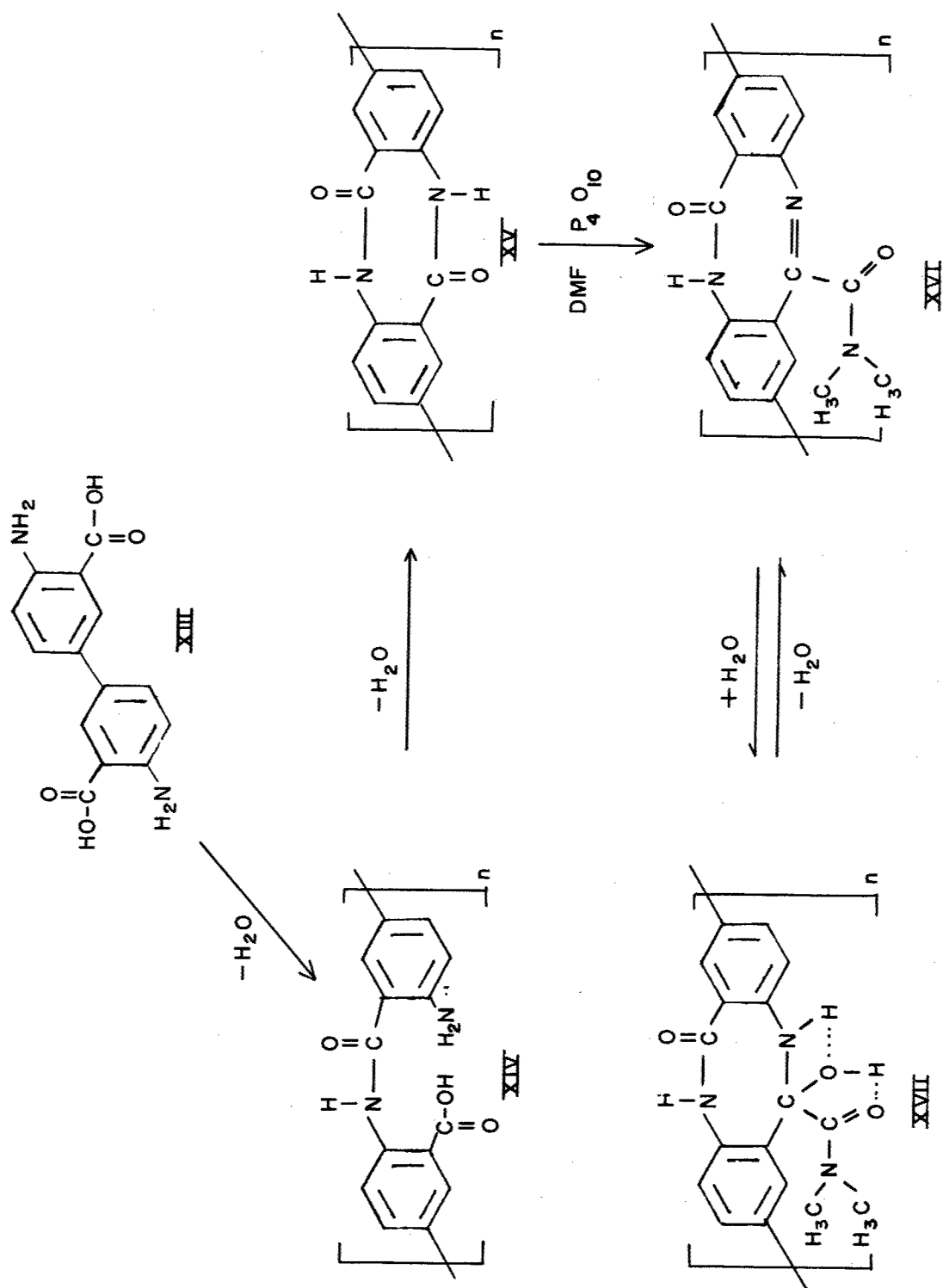


Figure 3 Polycondensation of Benzidine-3,3'-dicarboxylic Acid, XIII, with Dimethylformamide and Phosphorus Pentoxide

material, although swelled with solvent, would not readily dissolve even on prolonged heating. During this time any small amount of moisture absorbed during the operations, or water present as a result of incomplete dehydration of XVII, can be expected to enhance conditions favorable to chain scission. Successful spinning of fibers may be facilitated if the hydrated polymer, XVII, is first dried under moderated conditions, say, 100°C, and subsequently dissolved in methane sulfonic acid containing sufficient methane sulfonic anhydride to take up any excess water and give an anhydrous solution.

## SECTION III

### EXPERIMENTAL

#### A. General Comments

##### 1. Starting Materials

Anthranilic Acid, I, (Eastman No. 29), methyl anthranilate (Eastman No. 159) and benzonitrile (Eastman No. 487) were obtained from Distillation Products Industries, Rochester, New York, 14650.

2,5-diaminoterephthalic acid, VIII, was obtained by hydrolysis of the corresponding diethylester with aqueous alkali. Diethyl 2,5-diaminoterephthalate was obtained by oxidation of succinyl succinic acid and diethylester diimine with bromine in sulfuric acid. Succinyl succinic diethylester diimine was obtained by reaction of succinyl succinic acid diethylester in molten ammonium acetate (Reference 17). Succinyl succinic acid diethylester was obtained by cyclization of diethyl succinate with sodium ethylate (References 17 and 18).

Benzidine-3,3'-dicarboxylic acid, XIII, was prepared from hydrazobenzene dicarboxylic acid by heating with hydrochloric acid (Reference 19). Hydrazobenzene dicarboxylic acid was obtained from *o*-nitrobenzoic acid by the method of Heller (Reference 20).

##### 2. Infrared Spectra

The infrared spectra were obtained by use of a Perkin Elmer Model 137 Infrared Spectrophotometer.

##### 3. Thermogravimetric Analyses

Thermogravimetric analyses were obtained by heating 50 to 100 mg. of the compound under nitrogen in a Chevenard Thermobalance (Adamel, Paris, France) to 900°C at a heating rate of 180°C per hour.

#### 4. High Resolution Mass Spectrometry

The compounds were introduced via the direct introduction probe at temperatures between 200 and 250°C depending on the run, into a CEC Model 21-100B Mass Spectrometer at an ionizing voltage of 70eV and at an accelerating voltage of 8kV.

#### B. Model Reactions

1. Condensation of Anthranilic Acid, I, in Dimethylformamide with phosphorous pentoxide.

A solution was prepared from 6g of anthranilic acid, I, and 750 ml of dimethylformamide. 100g of powdered phosphorous pentoxide was added in small portions. The temperature rose from 27 to 33°C. The reaction mixture was stirred over the 72 hours at room temperature. It still contained solid material. The temperature was raised to 60°C and stirred for 24 hours at this temperature. The reaction mixture became a clear yellow solution with no undissolved phosphorous pentoxide present. The solution was stirred to 70°C for 24 hours, at 80°C for 24 hours, and at 90°C for one hour. The solution was cooled and added slowly with stirring to two liters of benzene. The solvent mixture (DMF and benzene) was decanted from the small amount of white gummy residue on the bottom of the flask, and allowed to evaporate slowly in the hood, at 80°C to a gummy residue. This residue was soluble in methanol and in benzene. It was dissolved in 100 ml of warm benzene. The solution was treated with charcoal and filtered. The filtrate was added slowly to 200 ml of hexane giving a white precipitate. Yield, 2.3g mp 137°C. The sample was recrystallized from 250 ml of boiling ligroin (bp 90 to 120°C). Yield, 2.2g, mp 137°C. The compound was dried at 120°C/0.1 mm for 3 hours. It was soluble in chloroform and in carbon tetrachloride. Its infrared spectra are shown in Figures 4 and 5. Its molecular weight, VP0/benzene was found to be 310. Its mass spectrum (Figure 6) exhibits the molecular ion constant at m/e 293 with significant peaks at m/e, 249, 211, 130, 102, 90, 76, 44, 28, and 15. Its NMR spectra are shown in Figures 7 and 8.



Anal. Calc'd. for  $C_{17}H_{15}O_2N_3$ , IV: %C, 69.61; %H, 5.16; %O, 10.91, %N, 14.37, Mol Wt, 293  
 Found %C, 69.71; %H, 5.24; %O<sup>U</sup>, 11.35; %N<sup>D</sup>, 14.17, Mol Wt,\* 310; m/e 293

U - oxygen by the Untersaucher method

D - nitrogen by the Dumas method

\* - molecular weight by the VPO method in benzene

2. Reaction of dibenzo-[b,f] [1,5]-diazocine-6,12, [5H, 11H]-dione, III, with dimethylformamide in the presence of  $P_2O_5$

A solution of 2.38g of dibenzo-[b,f] [1,5]-diazocine-6,12, [5H, 11H]-dione, III, in 150 ml of dimethylformamide was added to a suspension of 40g of phosphorus pentoxide in 50 ml of dimethylformamide with stirring at room temperature. After four hours, the temperature was raised to 50°C and stirred for 18 hours at this temperature. At this point an appreciable amount of phosphorus pentoxide remained undissolved. The temperature was raised to 70°C where it was maintained six hours. The mixture was poured into one liter of benzene. The benzene layer was decanted and evaporated in the hood to a tacky residue. This was recrystallized from ligroin (bp 90 to 120°C) as white needles, mp 137°C. Yield 1.6g. Its infrared spectrum (Figure 9) is identical with that obtained from the product, IV, (Figure 4).

## C. Polycondensations

### 1. General Procedures

a. Condensation polymerization of 2,5-diaminoterephthalic acid, VIII, with dimethylformamide and phosphorus pentoxide

1) In a Solution of Phosphorous Pentoxide Dissolved in Dimethylformamide

The phosphorous pentoxide was added to the dimethylformamide in a three necked flask fitted with a stirrer, adapter, and inlet tube for

nitrogen, and a reflux condenser. The suspension was stirred in a nitrogen atmosphere, heated up to 120°C and maintained at this temperature until all of the phosphorous pentoxide had dissolved.

Next the powdered monomer was added to the solution in small portions with stirring at the temperature indicated, and the reaction mixture was stirred under the temperature conditions and for the time indicated in Table III. The reaction product was a spongy brown polymer which settled out of the reaction mixture. It was isolated by one of the methods indicated below.

a) The supernatant solvent mixture was decanted from the spongy polymer, and the polymer was washed initially with a suitable volume of water (usually several 100 ml to 500 ml portions, depending on the size of the batch being run). The washed polymer was neutralized with dilute aqueous sodium bicarbonate or ammonium hydroxide solution, then washed with water, dilute acetic acid, additional water, and lastly with a low boiling solvent such as methanol, ethanol, or acetone.

b) The reaction mixture was treated with an equal volume of benzene and decanted. At least another two benzene washes were employed to "leach out" most of the dimethylformamide. Usually a small amount of polymeric product separated from the combined benzene washes on standing. The polymer remaining in the flask was quite spongy, and became an opaque tan granular material on treatment with water or methanol which was filtered off. The crude product at this point still contained an appreciable amount of phosphorus. As indicated above, the crude polymer was washed with water and neutralized with dilute aqueous sodium bicarbonate or ammonium hydroxide and further washed with water, dilute acetic acid, and solvents such as methanol, ethyl alcohol, acetone, or benzene.

## 2) In a Suspension of Powdered Phosphorous Pentoxide in Dimethylformamide

The phosphorous pentoxide was added slowly while stirring to the dimethylformamide at room temperature. The solid monomer was then added in small portions with stirring, or a solution of the monomer (usually as the sulfate) in dimethylformamide was added slowly from a dropping funnel. The reaction mixture was stirred under the temperature conditions and for the time indicated in Table III.

The procedures are tabulated in Tables III and IV. A comparison of the analytical results with properties of the polymers is shown in Table IV.

The product was subjected in some cases with further "purification" steps which involve extraction by soaking in a solvent, or by Soxhlet extraction. Usually the solvent was alcohol, benzene, tetrahydrofuran, dioxane, or dimethylformamide. When dimethylformamide was used, it usually resulted in removal of low molecular weight soluble material, which was recovered by addition of the solution to benzene.

### b. Condensation Polymerization of Benzidine-3,3'-dicarboxylic acid with Dimethylformamide and Phosphorus Pentoxide.

#### 1) Preparation of the Polymers

##### a) Polycondensation of the Monomer in a Solution of Phosphorus Pentoxide in Dimethylformamide.

A solution of phosphorus pentoxide in dimethylformamide was prepared by adding powdered phosphorus pentoxide to the solvent while stirring at room temperature and gradually raising the temperature to 120°C when solution was completed. The time required for solution varied from several hours to several days depending on the size of the batch,

TABLE III  
POLYCONDENSATION OF 2,5-DIAMINOTEREPHTHALIC ACID,  
VII, AND DIMETHYLFORMAMIDE WITH PHOSPHOROUS PENTOXIDE

Run No.	Monomer g.	P <sub>4</sub> O <sub>10</sub> g.	DMF ml.	Preparation Procedure	Temp. °C	Time Hrs.	Yield g.	Solubility			Viscosity $\eta_{inh}$ .	Mol. Wt.
								DMF	H <sub>2</sub> SO <sub>4</sub>	CH <sub>3</sub> SO <sub>3</sub> H		
A	0.90	25	200	(1)(a)1	100°-120°	72	-	-	S	S	0.14 <sup>a</sup>	-
B	3.92	50	300	(1)(a)2	90°-100°	96	1.76	S	S	S	-	4920 <sup>x</sup>
							2.35	i	S/S	S	0.26 <sup>a</sup>	-
C	49	100	750	(1)(b)	60°	192	5.85				0.54 <sup>b</sup>	6600 <sup>x</sup>
											0.19 <sup>c</sup>	
											0.58 <sup>b</sup>	4900 <sup>x</sup>
											0.21 <sup>c</sup>	



a. inherent viscosity in conc. sulfuric acid

b. inherent viscosity in methane sulfonic acid

c. inherent viscosity in dimethylformamide

x. molecular weight by the VPO method in dimethylformamide

TABLE IV  
COMPARISON OF ANALYTICAL RESULTS WITH PROPERTIES OF THE POLYMERS FROM  
POLYCONDENSATION OF 2,5-DIAMINOTEREPHTHALIC ACID, VIII,  
WITH DIMETHYLFORMAMIDE AND PHOSPHORUS PENTOXIDE

Run No.	PROCEDURES	DRYING				ANALYSES						Vis- cosity $\eta_{inh}$	Mol. Wt.							
						%C	%H	%N	%P	%S	%ash									
A	Prep- aration Isola- tion	Purifi- cation	Time	Temp	Pres- sure	Calc'd for $C_{22}H_{18}O_4N_6, XI$	Found	61.39	4.22	19.53	none	none								
								hrs	°C	mm	Calc'd for $C_{22}H_{22}O_6N_6, XII$	56.67			4.75	18.02	none	none		
								air dried	53.99	4.23	16.24	2.71			--	--	0.14 <sup>a</sup>	--	--	
B	B-2	C	wash soxhlet extract	16	80°	0.15	Found	57.44	4.98	18.39	0.22	--	--	4920						
								24	80°	0.05	Found	56.73	4.70	17.68	0.23	--	--	0.26 <sup>a</sup>	--	--
C	B-1	C	soxhlet extract	24	180°	0.05	Found	60.72	5.10	18.00	trace	0.37	--	0.54 <sup>b</sup> 0.19 <sup>c</sup>	6600 <sup>x</sup>					
								24	180°	0.05	Found	61.15	4.74	18.06	trace	0.26	--	0.58 <sup>b</sup>	4900 <sup>x</sup>	
								24	180°	0.10	Found	59.79	4.39	19.36	--	--	--	0.21 <sup>c</sup>	--	--
								24	300°	0.03	Found	57.97	3.96	11.84	trace	trace	--	cross linked	--	--

concentration, and temperature. The resulting solution varied in color from a light orange yellow to a deep red depending upon the amount of phosphorous pentoxide and on the quantity of solvent used.

The monomer was added gradually either as a powdered solid or as a solution of the amino acid or its disulfate in dimethylformamide. The reaction mixture was stirred and heated under nitrogen at the temperatures and for the lengths of time indicated in Tables V and VI.

b) Polycondensation of the Monomer or its Disulfate in Solution with a Suspension of Phosphorus Pentoxide in Dimethylformamide.

Powdered phosphorus pentoxide was added to a solution of the amino acid or its disulfate and the reaction mixture was stirred under nitrogen at the temperature and for the length of time indicated in Tables V and VI.

2) Isolation of the Polymers

The reaction mixture usually consists of a suspension of spongy resinous material in the solvent. A certain amount of lower molecular weight material remains dissolved in solution "complexed" with phosphorus pentoxide. The spongy insoluble resinous product appears to be a complex of high molecular weight polymer, phosphorus pentoxide and dimethylformamide.

a) The solvent containing the lower molecular weight polymer "complexed" with phosphorus pentoxide was decanted from the spongy material and added slowly with stirring to a large excess of benzene. This resulted in precipitation of the low molecular weight polymer-phosphorous pentoxide complex as a yellow taffy-like material. The polymer itself was obtained as a light tan granular solid by stirring with water or cold methanol. The product was washed thoroughly with water and/or methanol, dried, first by suction, then in an oven at 100 to 120°C.

b) The spongy high molecular weight polymer complexed with dimethylformamide and phosphorus pentoxide was stirred with benzene to soak up the excess dimethylformamide and filtered. The complex was broken up by treatment with cold water and/or methanol resulting in formation of a tan granular solid which was filtered off, washed with water and dried in the usual manner.

### 3) Purification of the Polymer

At this point the polymer still contains an appreciable amount of phosphorus, from 0.5 to 2.0%, even after extensive washing of the precipitate with water and/or methanol. The percent ash varied between 2 and 6%. In order to obtain a polymer free of phosphorus and with a negligible ash content a variety of techniques were employed with varying success.

a) A very low molecular weight polymer which was soluble in dimethylformamide (i.e. MW = 950/VP0/DMF) was also found to be soluble in aqueous sodium bicarbonate. This solution was treated with charcoal and filtered. The polymer was reprecipitated with dilute acetic acid, washed with water and dried at 80°C/0.01 mm. Some phosphorus still present in the polymer and its ash content was appreciable. Analytical results are shown in Table VI. (see Run [A]).

b) A medium molecular weight polymer, which was soluble in dimethylformamide (i.e. MW = 4375/VP0/DMF) was found to be insoluble in dilute aqueous sodium bicarbonate. It was washed with this reagent, followed by extensive washing with water and finally alcohol. Some phosphorus was present in this polymer, and its ash content was appreciable. Analytical results are shown in Table VI. (see Run [B]).

c) A high molecular weight polymer, insoluble in DMF, was soluble in cold concentrated sulfuric acid when its viscosity was below 0.5. Solubility in concentrated sulfuric acid usually decreased as molecular weight became higher. All of the high molecular weight polymers were soluble in methane sulfonic acid.

(1) Where the polymer was of moderately high molecular weight and still easily soluble in concentrated sulfuric acid it was first stirred with dimethylformamide at room temperature for 24 hours to remove any low molecular weight material. After filtration the material was washed on the filter consecutively with large volumes of water, dilute ammonium hydroxide solution, dilute acetic acid, water alcohol or methanol, and finally benzene. The polymer then was vacuum dried at 80 to 120°C/0.01 mm, or in some cases Soxhlet extracted with methanol for 24 hours before vacuum drying.

(2) Where the polymer was of high enough molecular weight to be soluble only in concentrated sulfuric acid with difficulty, or only partly soluble, the samples were stirred at room temperature in this acid, then filtered and treated as in c)(1) above.

(3) The highest molecular weight fractions which were insoluble in concentrated sulfuric acid after washing as in c)(2) above were dissolved with stirring in cold methane sulfonic acid. Sometimes warming was necessary. The solution was filtered through fritted glass and the filtrate was added dropwise to a large volume of methanol. The polymer was filtered off and washed with a large volume of methanol in small portions. This treatment usually removed all the phosphorus. Extensive washing was necessary to remove all the methane sulfonic acid. It was usually advisable to Soxhlet extract as in c)(1) above. The polymer then was vacuum dried.

The procedures used are referred to in Table V and a comparison of the analytical results with polymer properties is shown in Table VI.



TABLE V  
POLYCONDENSATION OF BENZIDINE-3,3'-DICARBOXYLIC ACID, XIII, WITH  
DIMETHYLFORMAMIDE AND PHOSPHORUS PENTOXIDE

Run No.	Monomer g.	P <sub>4</sub> O <sub>10</sub> g.	DMF ml.	Preparation Procedure	Temp. °C	Time Hrs.	Yield g.	Solubility			Viscosity $\eta_{inh}$	Mol. Wt.
								DMF	H <sub>2</sub> SO <sub>4</sub>	CH <sub>3</sub> SO <sub>3</sub> H		
A	4.08	10	300	1.	70° 100°	18	1.23	S	-	-	-	950
						96						
B	4.08	50	300	1.	90°	96	2.80	i	p.s.h	S	0.40 <sup>a</sup>	4375
							1.10	S	-	-	-	
C	4.11	75	600	1.	90°	20						-
					120°	20						
					150°	3 1/2						
					120°	16		-	ic	-	-	
D	4.11	100	300	1.	100°	48	1.36	S	S	S	-	-
					120°	144	3.88	-	i	-	-	-
E	6.8 (as the disulfate)	100	750	2.	60°	144	5.8	i	p.s	S	1.04 <sup>b</sup> 1.44 <sup>b</sup>	-
							1.22	S	S	S	0.18	

TABLE V (CONTINUED)

Run No.	Monomer g.	P <sub>4</sub> O <sub>10</sub> g.	DMF ml.	Preparation Procedure	Temp. °C	Time Hrs.	Yield g.	Solubility			Viscosity $\eta_{inh}$	Mol. Wt.
								DMF	H <sub>2</sub> SO <sub>4</sub>	CH <sub>3</sub> SO <sub>3</sub> H		
F	6.8	100	750	2	27° 50°-80°	72	3.80	S	S	S	0.38 <sup>b</sup>	—
						96	2.26	i	p.s.	S	2.35 <sup>b</sup>	—
G	19.06	500	2100	2	60° 65°-70° 80° 90°	27						—
						48	4.2	S	S	S	0.57 <sup>b</sup>	—
						24	15.4	i	p.s.	S	1.70 <sup>b</sup>	—
						24						—
H	10.88	260	2100	1	80°	96	10.82	i	S	S	0.36 <sup>b</sup>	—
I	5.40	200	300	2	27° 60° 80°	24	4.35	i	S	S	0.15 <sup>b</sup>	—
						18						—
						4						—
J	13.1	600	250 plus 1000 dioxane	2	60° 70°-90° 90°	24						—
						5	8.36	i	S	S	0.14 <sup>b</sup>	—
						24						—
K	13.1	500	500	2	150°	18	17.1	i	i	i	—	—

a. Viscosity in conc. sulfuric acid  
b. Viscosity in methane sulfonic acid

TABLE VI

COMPARISON OF ANALYTICAL RESULTS WITH PROPERTIES OF THE POLYMERS FROM  
POLYCONDENSATION OF BENZIDINE-3,3'-DICARBOXYLIC ACID, XIII, WITH  
DIMETHYLFORMAMIDE AND PHOSPHORUS PENTOXIDE

Run No.	PROCEDURES			DRYING			ANALYSES							Vis- cosity $\eta_{inh}$	Mol. Wt.
							%C	%H	%N	%P	%S	%ash			
	Prep- aration	Isola- tion	Purifi- cation	Time hrs	Temp °C	Pres- sure mm	Calc'd for ( $C_{17}H_{15}O_3N_3$ ) XVI								
							Calc'd for ( $C_{17}H_{13}O_2N_3$ ) XVI								
[A]	(a)1	(b)1	(c)1	16	100	0.10	Found	65.30	4.60	12.60	0.85	-	1.79	-	950 <sup>x</sup>
	(a)1	(b)1	(c)1	16	80	0.01	Found	65.38	4.67	13.65	0.53	-	1.79	-	4375 <sup>x</sup>
[B]		(b)2	(c)1	16	80	0.01	Found	63.79	4.71	13.13	1.52	-	1.86	0.40 <sup>b</sup>	-
	(a)1	(b)1	(c)1	16	100	0.01	Found	62.58	4.92	12.64	1.73	negl	5.87	-	-
[C]		(b)2	(c)3a	16	100	0.01	Found	66.49	4.90	13.08	0.13	negl	-	-	-
	(a)1	(b)1	(c)1	16	180	0.05	Found	64.74	4.58	12.63	0.80	negl	-	-	-
[D]		(b)2	(c)3a	16	180	0.05	Found	61.71	4.57	11.75	2.19	0.30	-	-	-
		(b)1	(c)1	16	180	0.05	Found	59.92	4.88	11.84	5.14	1.25	-	1.06	-
[E]	(a)2	(b)2	(c)3a	16	180	0.05	Found	66.30	4.70	13.18	0.00	0.00	0.00	1.44	-
		(b)2	(c)3c	16	180	0.05	Found	56.09	4.80	11.60	6.55	1.62	-	0.18	-

TABLE VI (CONTINUED)

Run No.	PROCEDURES			DRYING			ANALYSES							Vis- cosity $\eta_{inh}$	Mol. Wt.				
							%C	%H	%N	%P	%S	%ash							
[F]	(a)2	Prep-Isola- tion	Purifi- cation	Time	Temp	Pres- sure	Calc'd for	66.01	4.89	13.58	none	none	/						
							(C <sub>17</sub> H <sub>15</sub> O <sub>3</sub> N <sub>3</sub> ) XVI	none											
		(b)1	(c)1, 3a	hrs	°C	mm	Calc'd for	70.09	4.55	14.42	none	none							
							(C <sub>17</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub> ) XVI	none											
							Found	66.89	5.35	13.18	-	-							
[G]	(a)2	(b)2	(c)3, c	16	180	0.01	Found	68.61	4.48	13.92	trace	0.49	none	2.35*					
							(c)3, b	24	120	0.01	Found	67.69	4.56	11.67	0.00	0.00	0.00	-	
		(b)1	(c)3, a	16	170	0.05	Found	66.81	4.71	11.02	0.00	0.00	0.00	0.57*					
							(c)3, a	18	150	0.01	Found	64.97	4.76	11.80	1.39	0.00	2.13	0.94*	
											(c)3, a	24	170	0.03	Found	66.39	4.97	12.23	0.00
(b)2				After heating 72 hours at 50° C in methane sulfonic acid											0.94				
[H]	(a)1	(b)2	(c)3, a	18	180	0.01	Found	66.19	4.56	12.26	0.00		0.00	1.70					
							(c)3, a	16	170	0.05	Found	66.26	4.78	13.40	0.00	0.53	0.00	-	
		(b)2	(c)3, b	16	110	0.10	Found	64.89	4.99	11.36	1.38	-	-	0.36					
							(a)2	(b)2	(c)1	16	100	0.10	Found	63.98	4.40	10.67	trace	-	0.15

TABLE VI (CONTINUED)

Run No.	PROCEDURES			DRYING			ANALYSES						Viscosity $\eta_{inh}$	Mol. Wt.
	Preparation	Isolation	Purification	Time	Temp	Pressure	Calc'd for	%C	%H	%N	%P	%S	%ash	
							(C <sub>17</sub> H <sub>15</sub> O <sub>3</sub> N <sub>3</sub> ) XVII	66.01	4.89	13.58	none	none	none	
							Calc'd for (C <sub>17</sub> H <sub>13</sub> O <sub>2</sub> N <sub>3</sub> ) XVI	70.09	4.55	14.42	none	none	none	
				hrs	°C	mm	Calc'd for (C <sub>14</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub> ) XIV	66.14	3.99	11.02	-	-	-	
[J]	(a)2	(b)2	(c)1	16	100	0.10	Found	65.42	4.47	9.53	1.02	-	-	0.14
[K]	(a)2	(b)2	(c)1	16	130	0.10	Found	58.69	4.98	11.71	0.48	0.77	1.10	cross-linked

Viscosities run at 0.5% in \* methane sulfonic acid;  $\phi$  conc. sulfuric acid; + dimethylformamide

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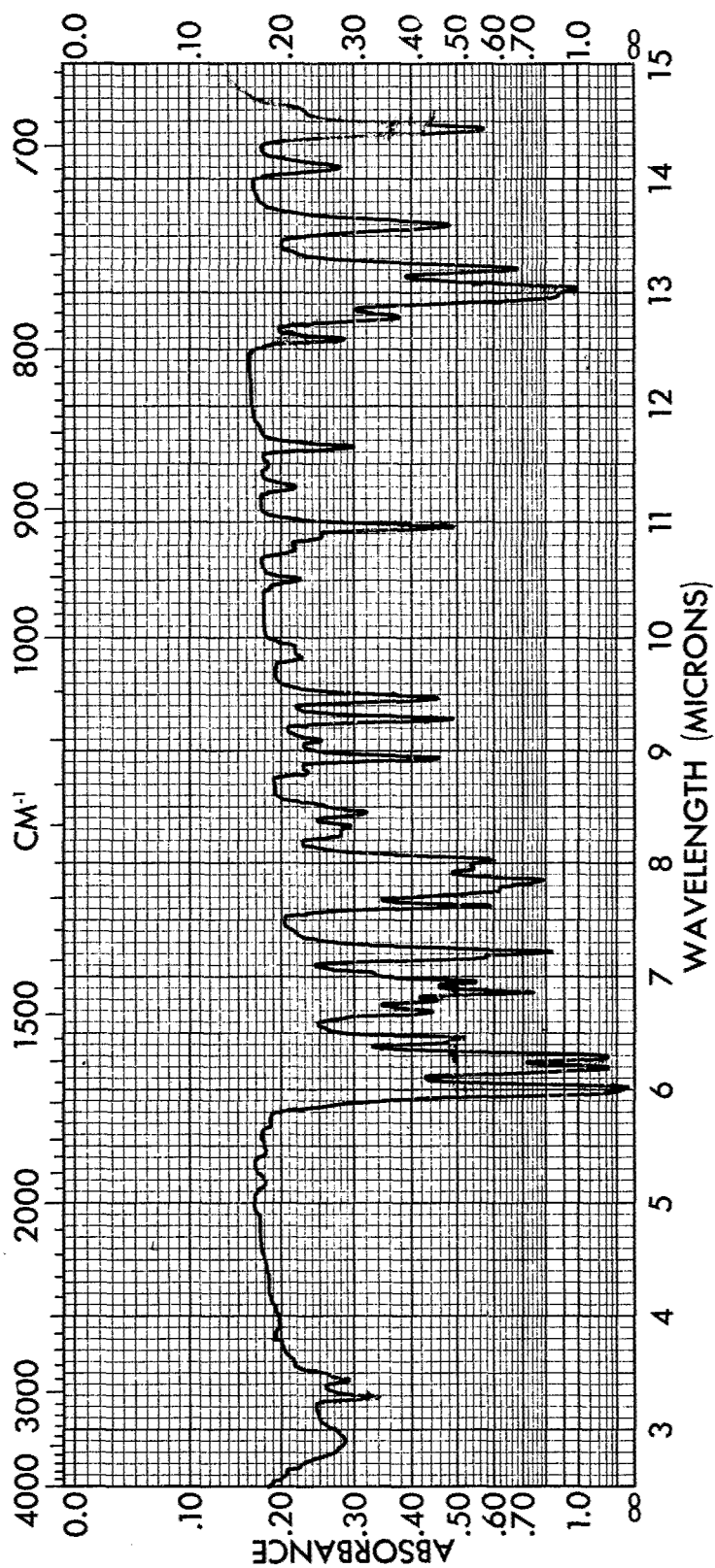


Figure 4 Infrared Spectrum of the Reaction Product of Anthranilic Acid, I, with Dimethylformamide, and Phosphorus Pentoxide (in KBr)

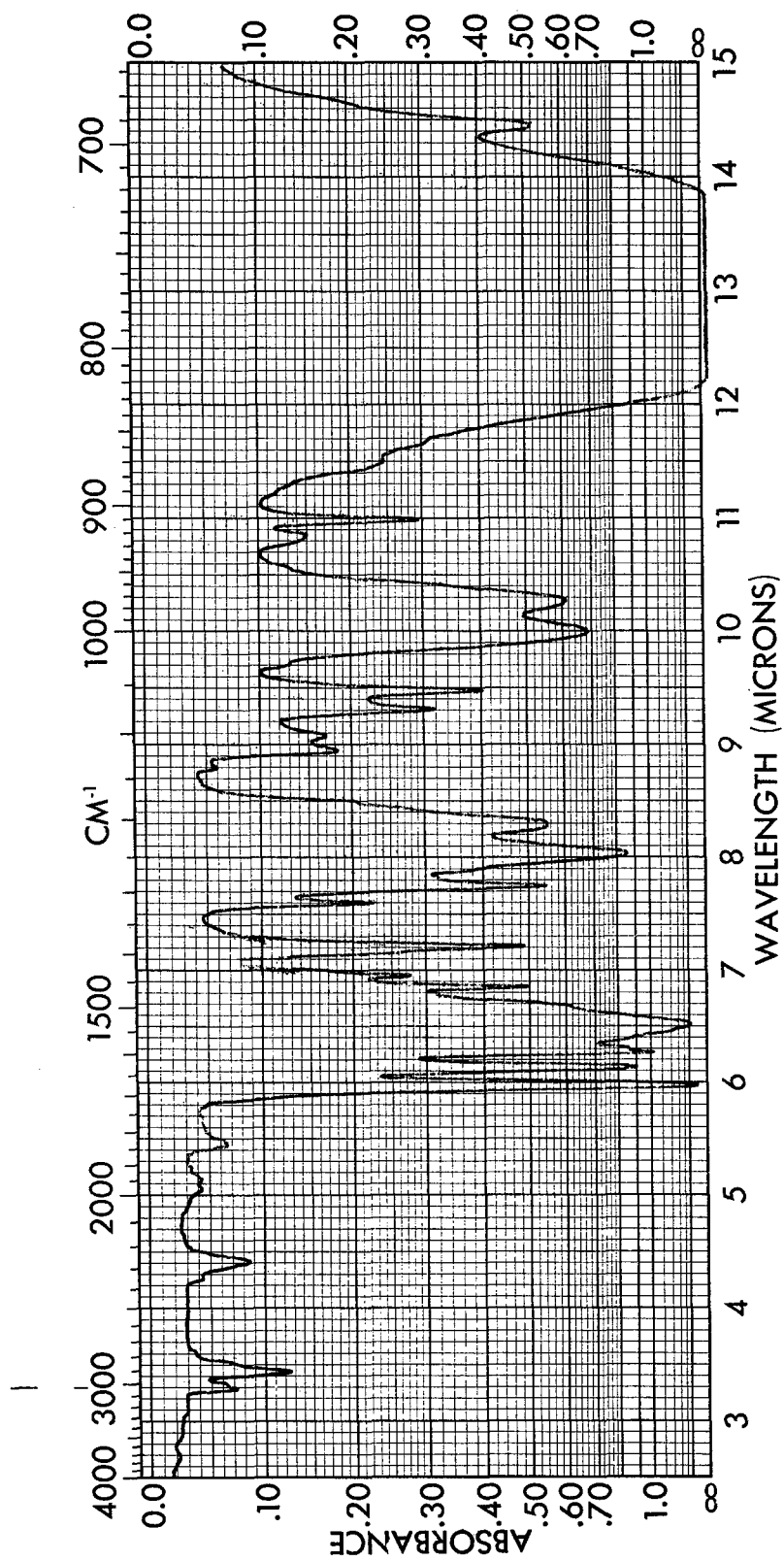


Figure 5 Infrared Spectrum of the Reaction Product of Anthranilic Acid, I, with Dimethylformamide and Phosphorus Pentoxide (in  $\text{CCl}_4$ )



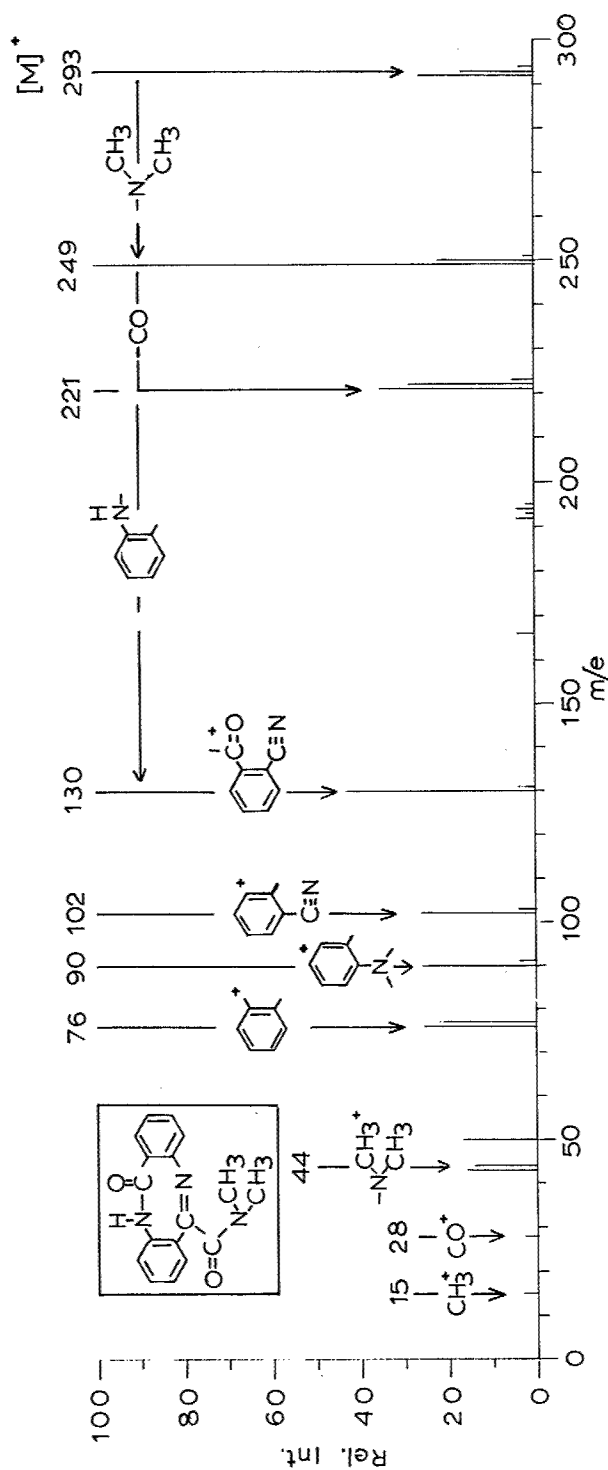


Figure 6 Mass Spectrum of the Reaction Product of Anthranilic Acid, I, with Dimethylformamide and Phosphorus Pentoxide

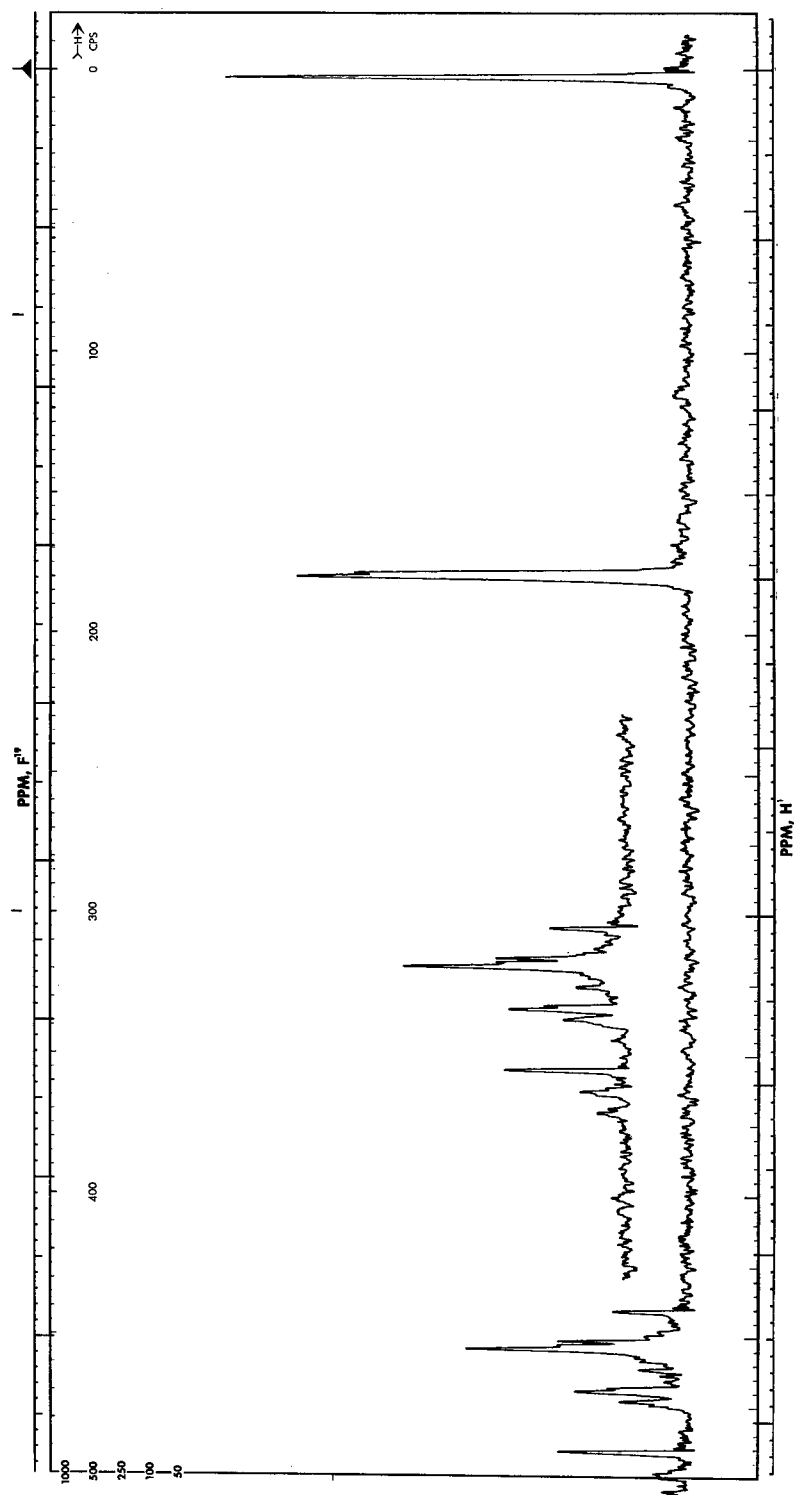


Figure 7 Nuclear Magnetic Resonance Spectrum of the Reaction Product of Anthranilic Acid, I, with Dimethylformamide and Phosphorus Pentoxide (run in  $\text{CDCl}_3$  at room temperature)

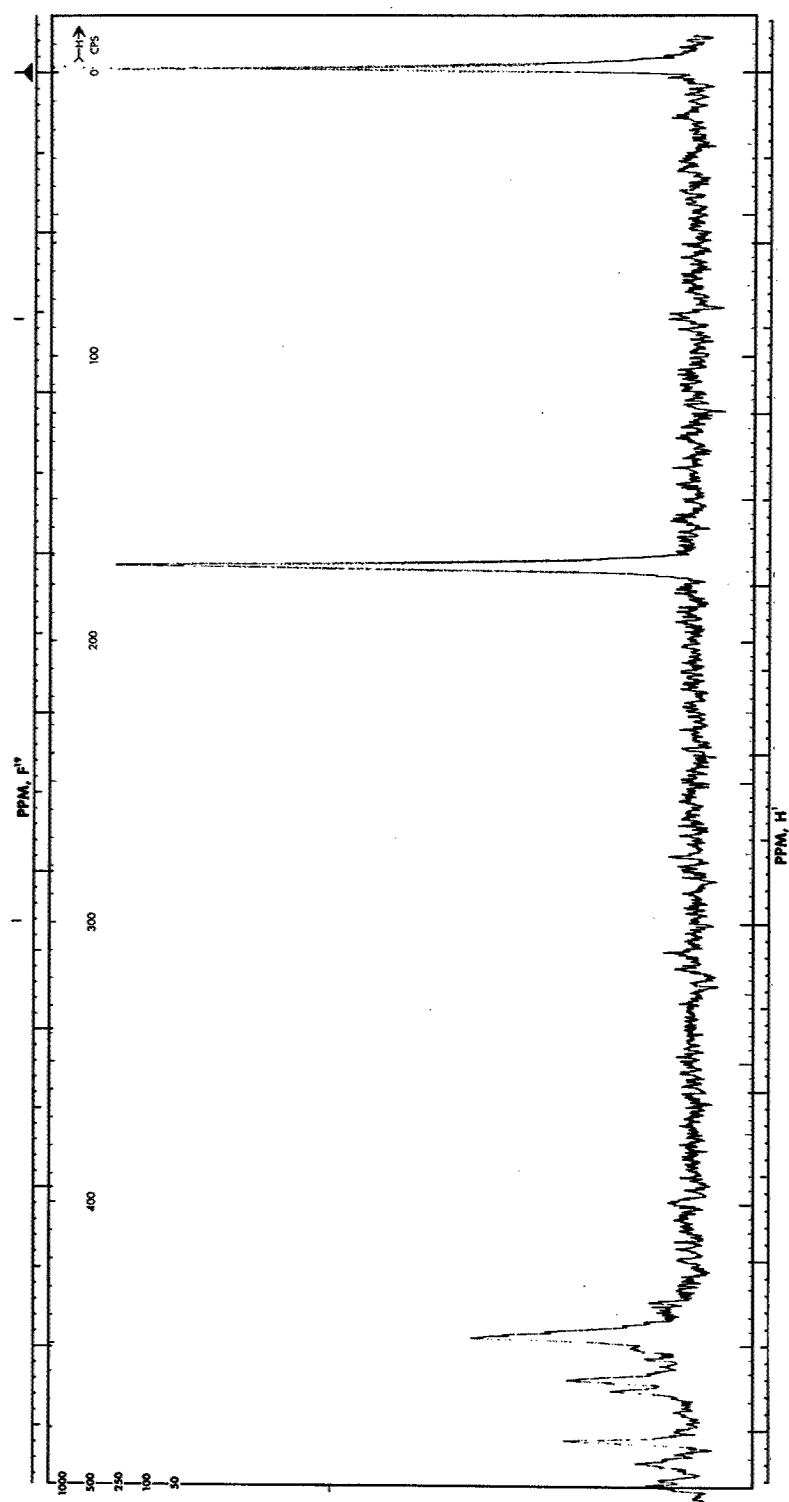


Figure 8 Nuclear Magnetic Resonance Spectrum of the Reaction Product of Anthranilic Acid, I, with Dimethylformamide and Phosphorus Pentoxide (run in  $\text{CDCl}_3$  at  $50^\circ \text{C}$ )

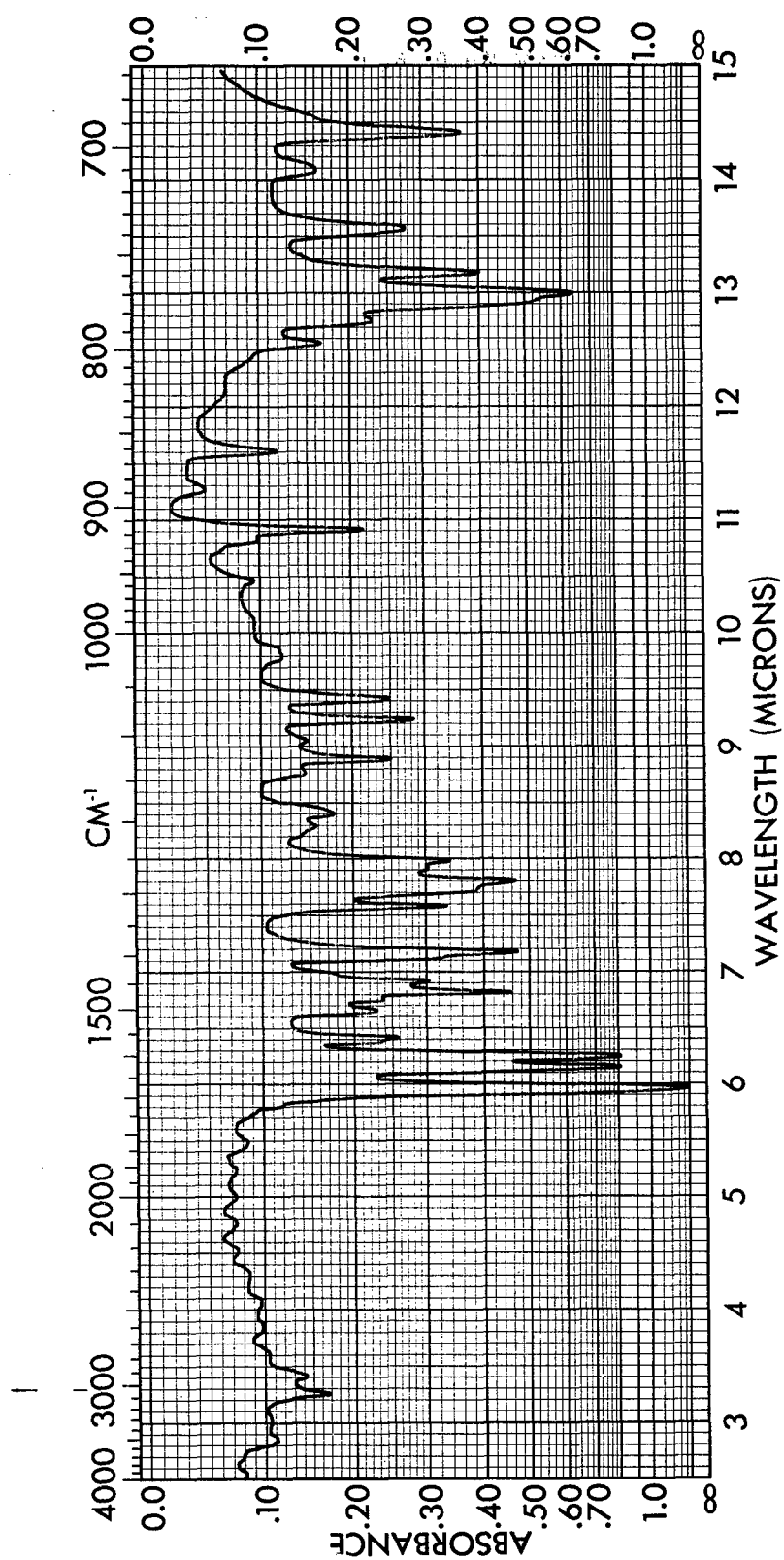


Figure 9 Infrared Spectrum of the Reaction Product of Dibenzo-[b,f] [1,5]-diazocine-6,12, [5H, 11H]-dione, III, with Dimethylformamide and Phosphorus Pentoxide (in KBr)

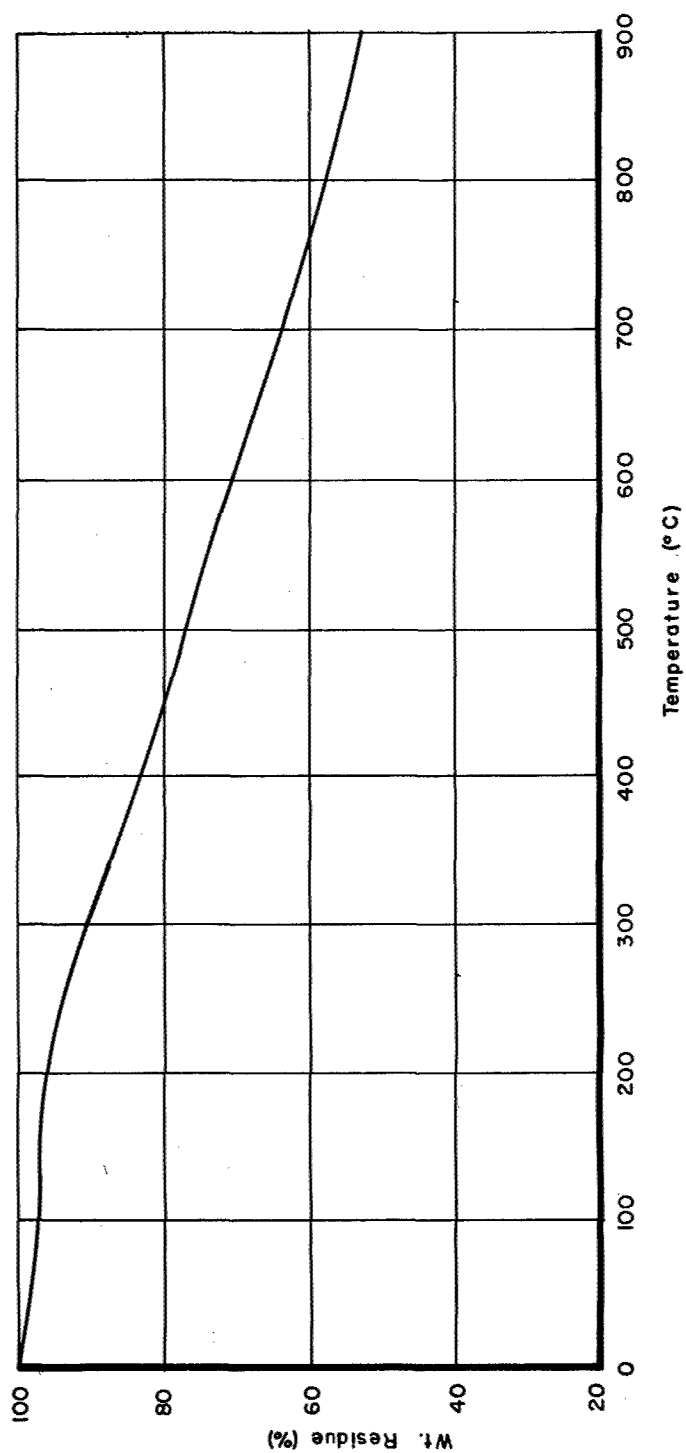


Figure 10 TGA Curve of the Polymer ( $C_{22}H_{22}O_6N_6$ ) $\eta$ , XII, ( $\eta_{inh} = 0.14$ ) from Polycondensation of 2,5-diamino-terephthalic Acid, VIII with Dimethylformamide and Phosphorus Pentoxide at 100 to 120°C (from run A)

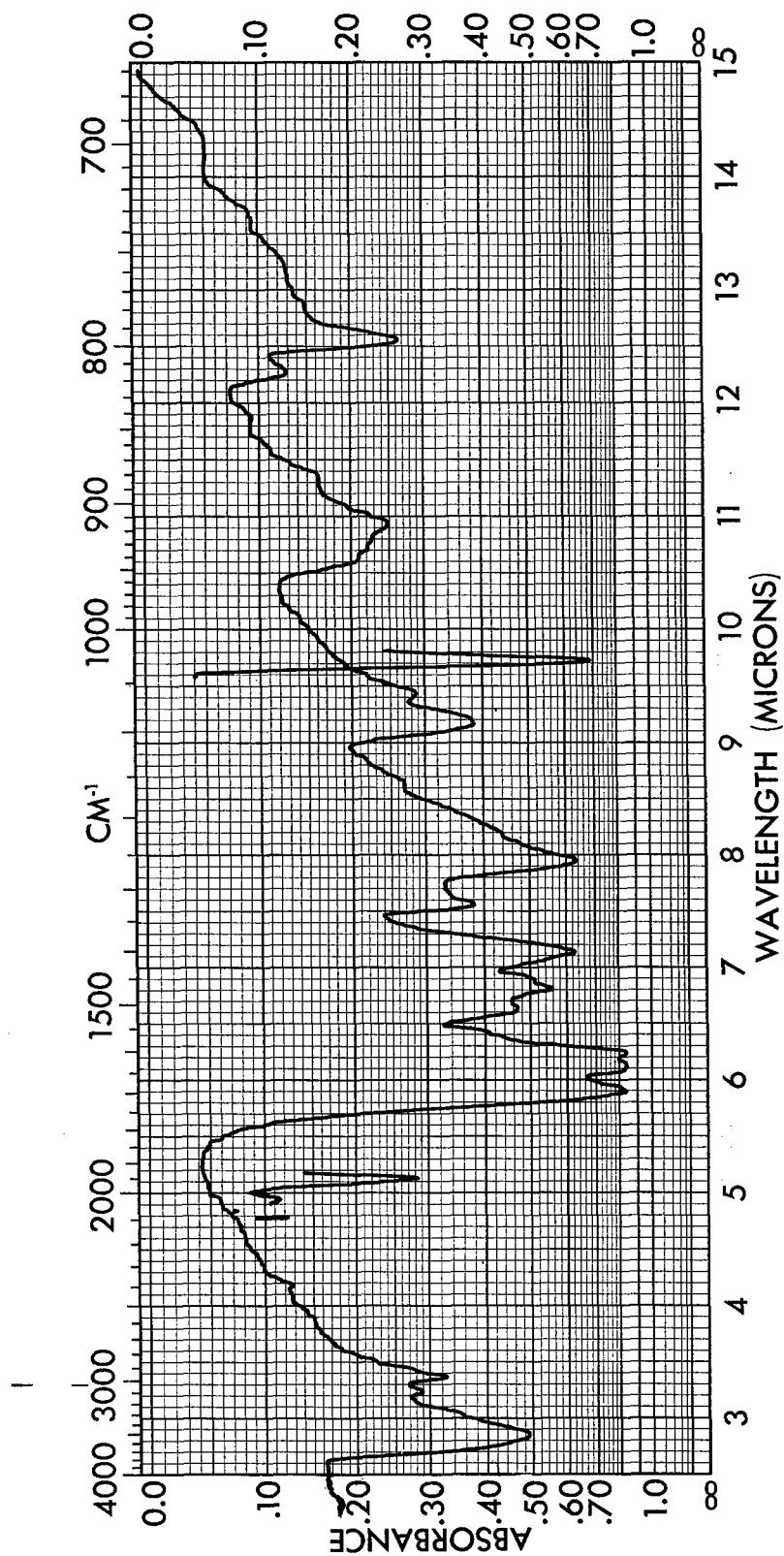


Figure 11 Infrared Spectrum of the Polymer ( $C_{22}H_{22}O_6N_6$ ) $\eta$ , XII, Mol. Wt. 4920) from Polycondensation of 2,5-diaminoterephthalic Acid, VIII, with Dimethylformamide and Phosphorus Pentoxide at 90 to 100°C (from run B)

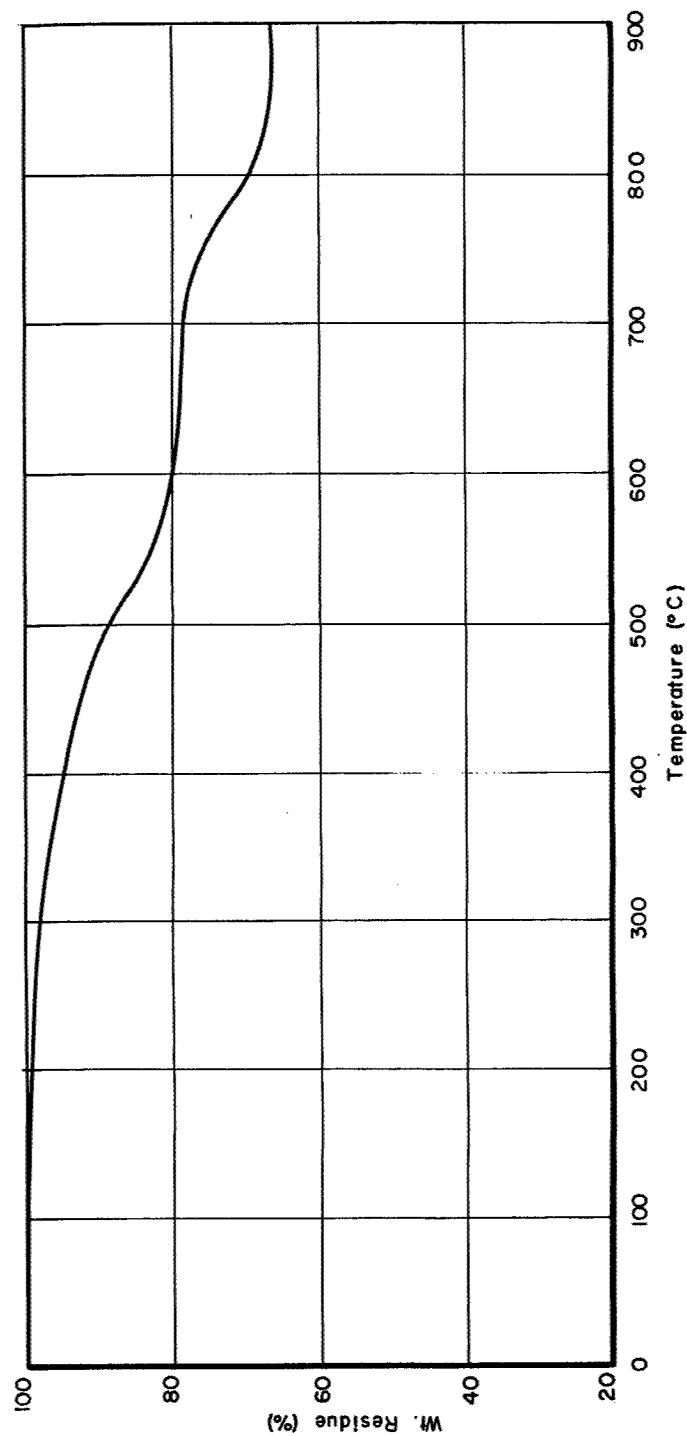


Figure 12 TGA Curve of the Polymer ( $C_{17}H_{15}O_3N_3$ ), XVII, ( $\eta_{inh} = 1.44$ ) from Polycondensation of Benzidine-3,3'-dicarboxylic Acid, XIII, with Dimethylformamide and Phosphorus Pentoxide (from run [E]).

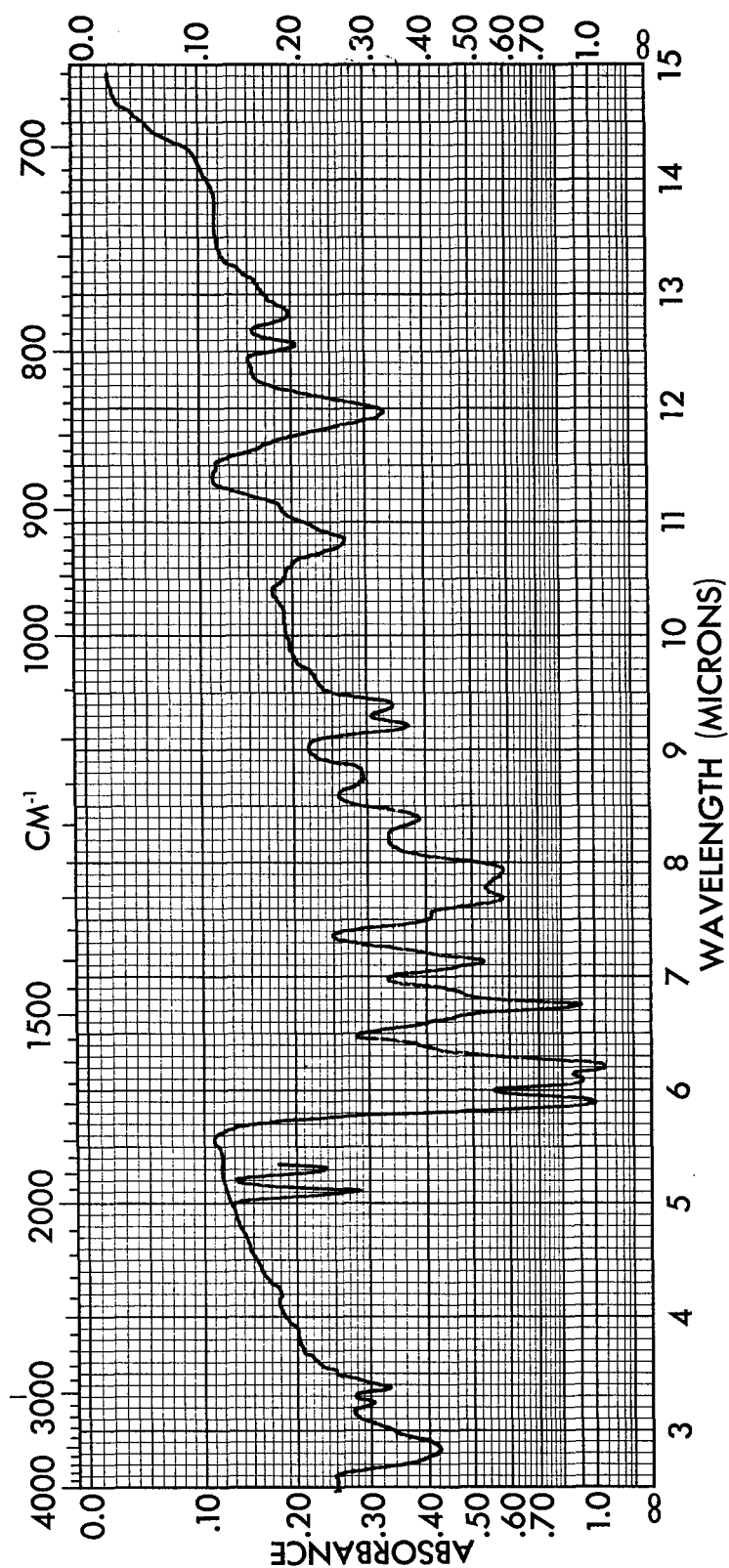


Figure 13 Infrared Spectrum of the Polymer ( $C_{17}H_{15}O_3N_3$ ), XVII,  
 ( $\eta_{inh} = 2.35$ ) from Polycondensation of Benzidine-3,3'-  
 dicarboxylic Acid., XIII, with Dimethylformamide and  
 Phosphorus Pentoxide (from run [F])



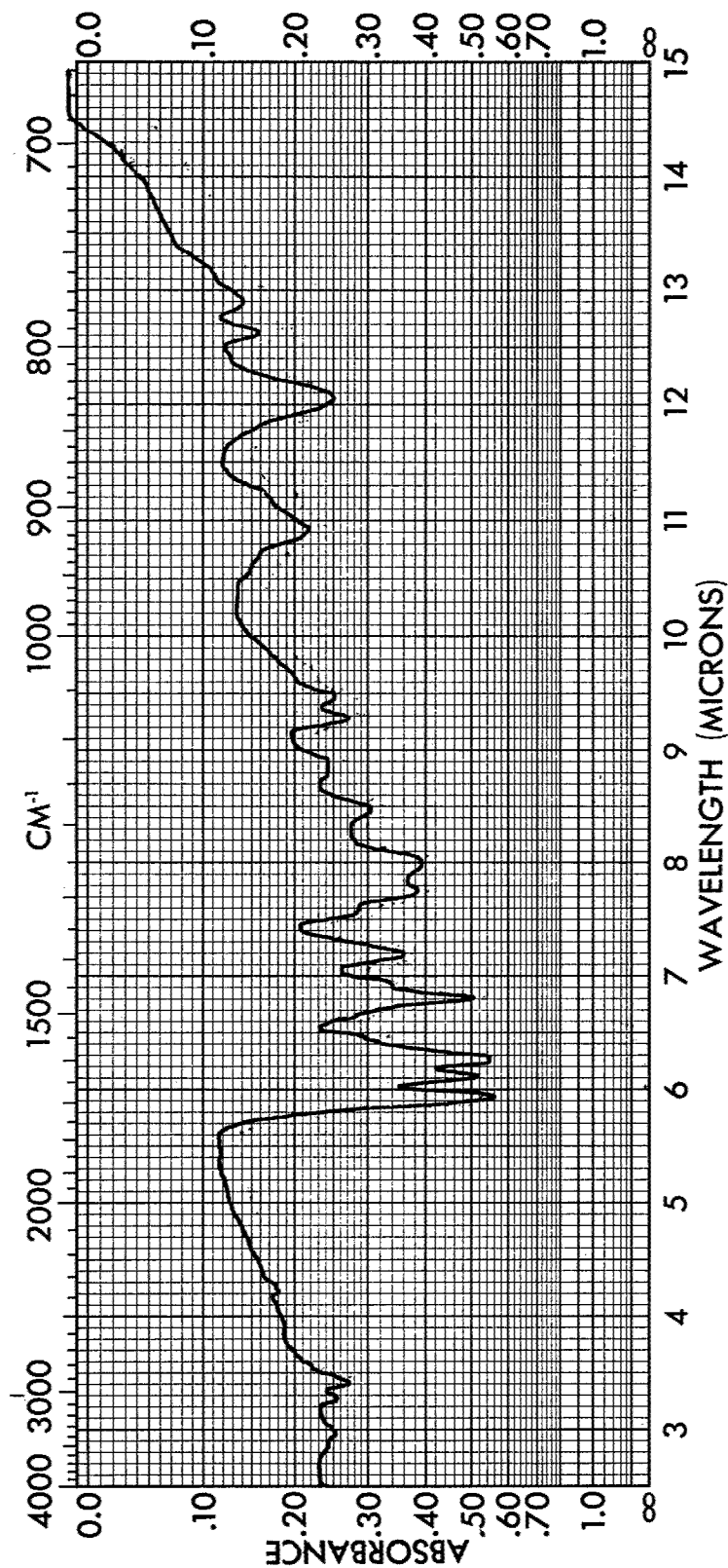


Figure 14 Infrared Spectrum of the Polymer ( $C_{17}H_{13}O_2N_3$ ), XVI, ( $\eta_{inh} = 2.35$ ) from Polycondensation of Benzidine-3,3'-dicarboxylic Acid, XIII, with Dimethylformamide, and Phosphorus Pentoxide (from fun [F]) (after Vacuum Drying KBr Window at 180°C/0.01 mm)

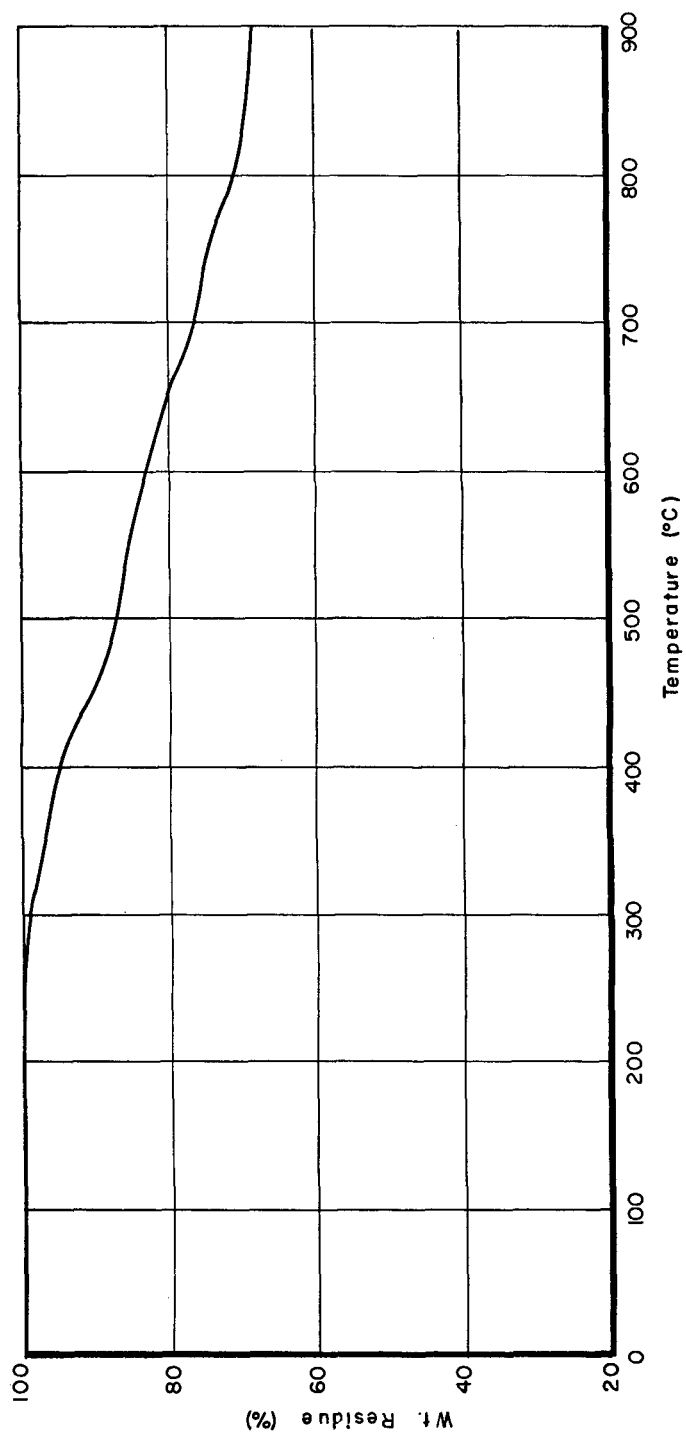


Figure 15 TGA Curve of the Polymer ( $C_{17}H_{13}O_2N_3$ ), XVI, ( $\eta_{inh} = 2.35$ )  
from Polycondensation of Benzidine-3,3'-dicarboxylic Acid,  
XIII, with Dimethylformamide and Phosphorus Pentoxide  
(from run [F])

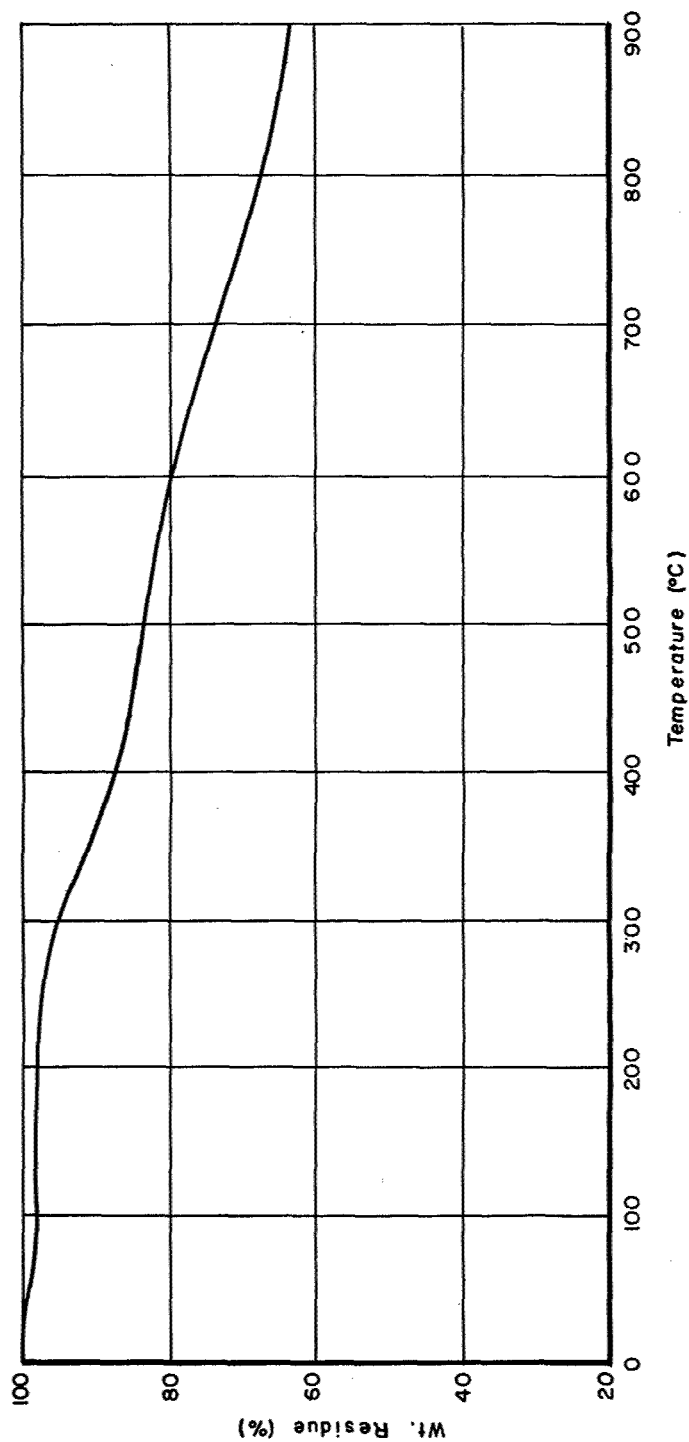


Figure 16 TGA Curve of the Polymer  $(C_{17}H_{15}O_3N_3)\eta$ , XVII, ( $\eta_{inh} = 0.94$ ) from Polycondensation of Benzidine-3,3'-dicarboxylic Acid, XIII, with Dimethylformamide and Phosphorus Pentoxide (from run [G])

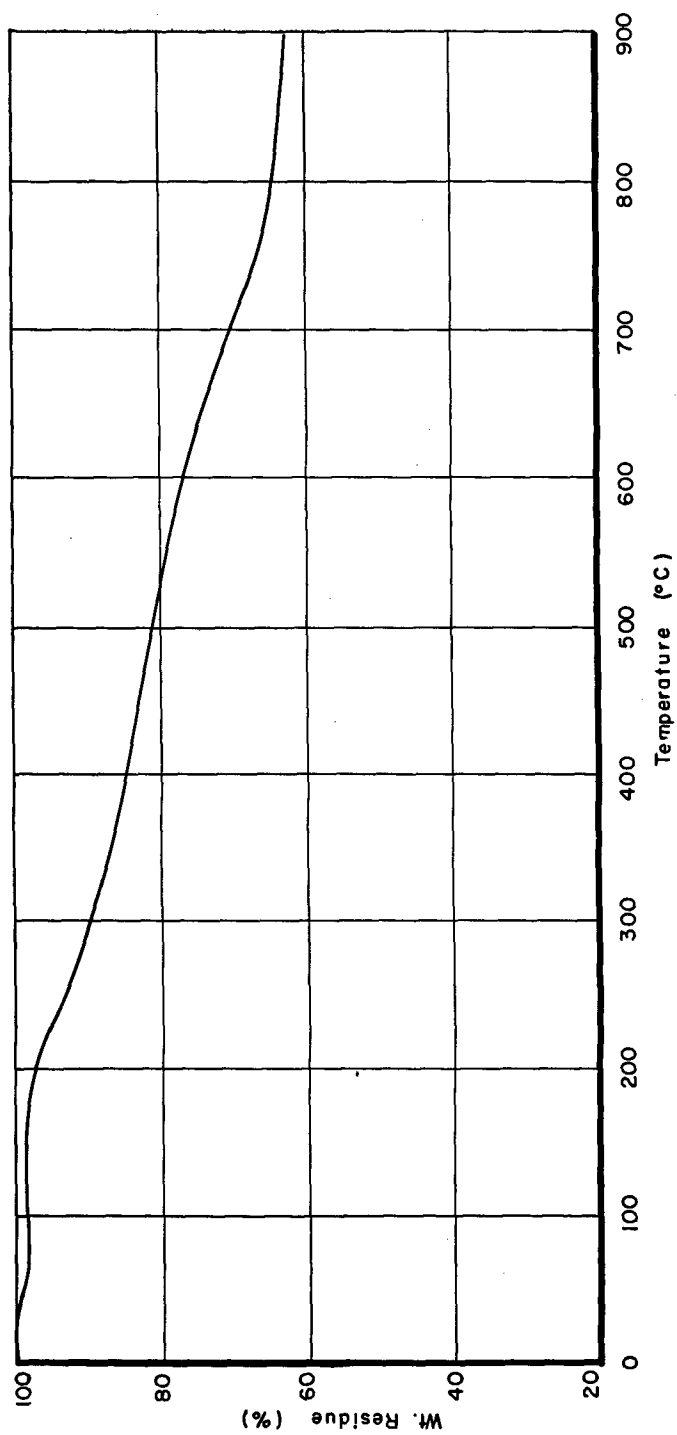


Figure 17 TGA Curve of the Crude Polymer, XVII, ( $\eta_{inh} = 0.15$ ) from Polycondensation of Benzidine-3,3'-dicarboxylic Acid, XIII, with Dimethylformamide and Phosphorus Pentoxide (from run [1])

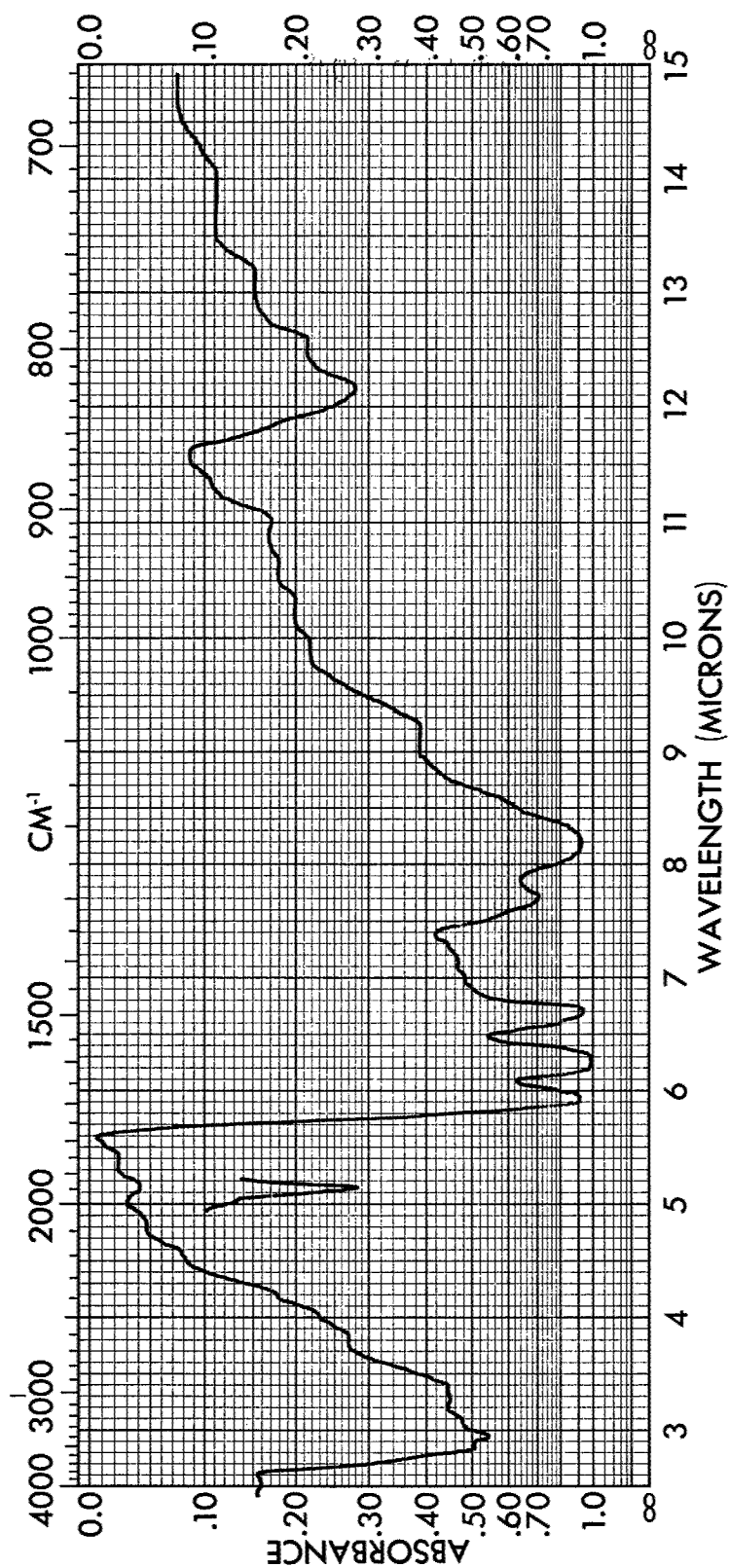


Figure 18 Infrared Spectrum of the Single Strand Polymer  
( $C_{14}H_{16}O_3N_2$ ), XIV, ( $\eta_{inh} = 0.14$ ) (from run [J])

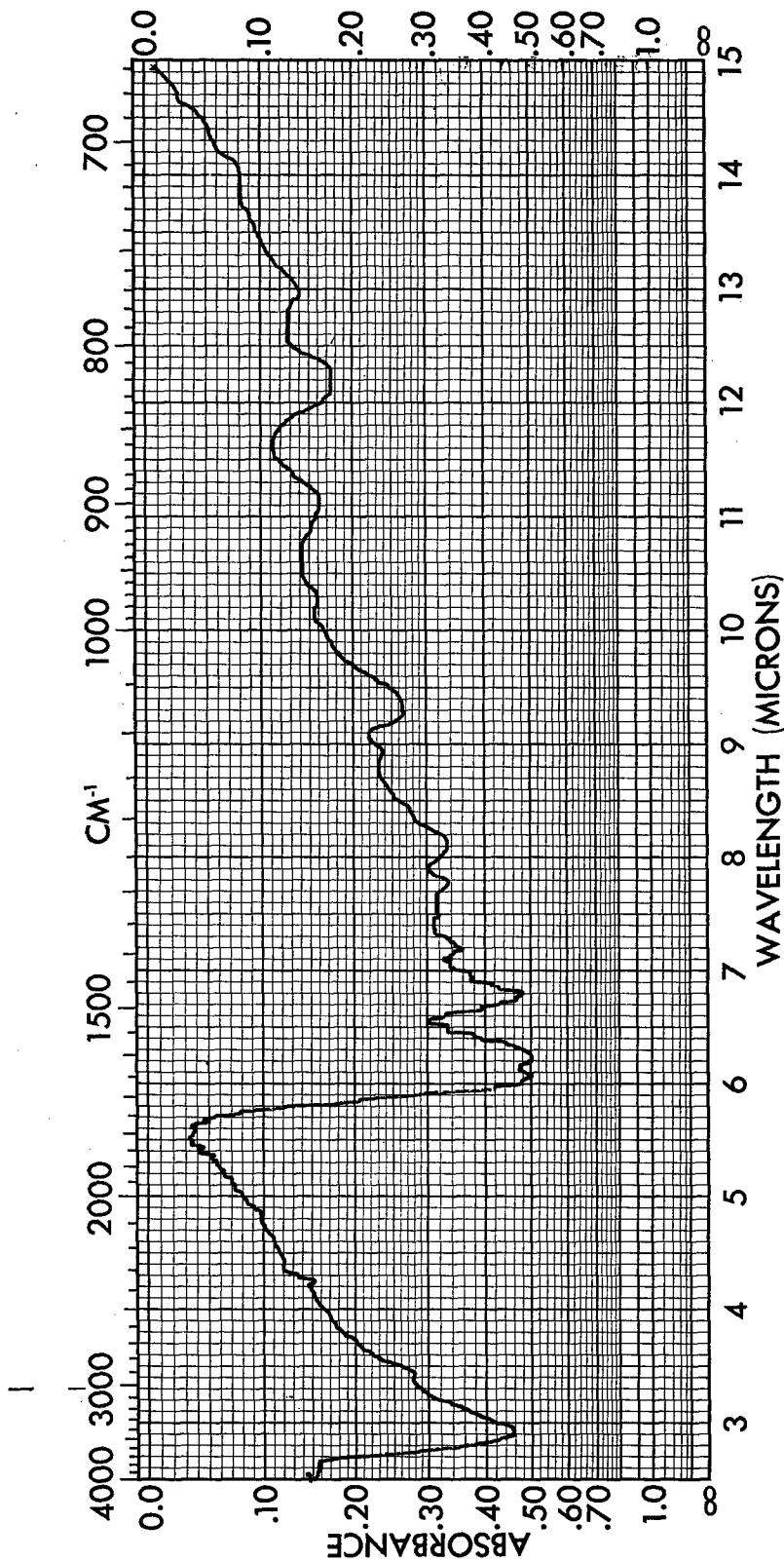


Figure 19 Infrared Spectrum of the Insoluble Polymer, (C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>N<sub>3</sub>), XVII, (from run [K])

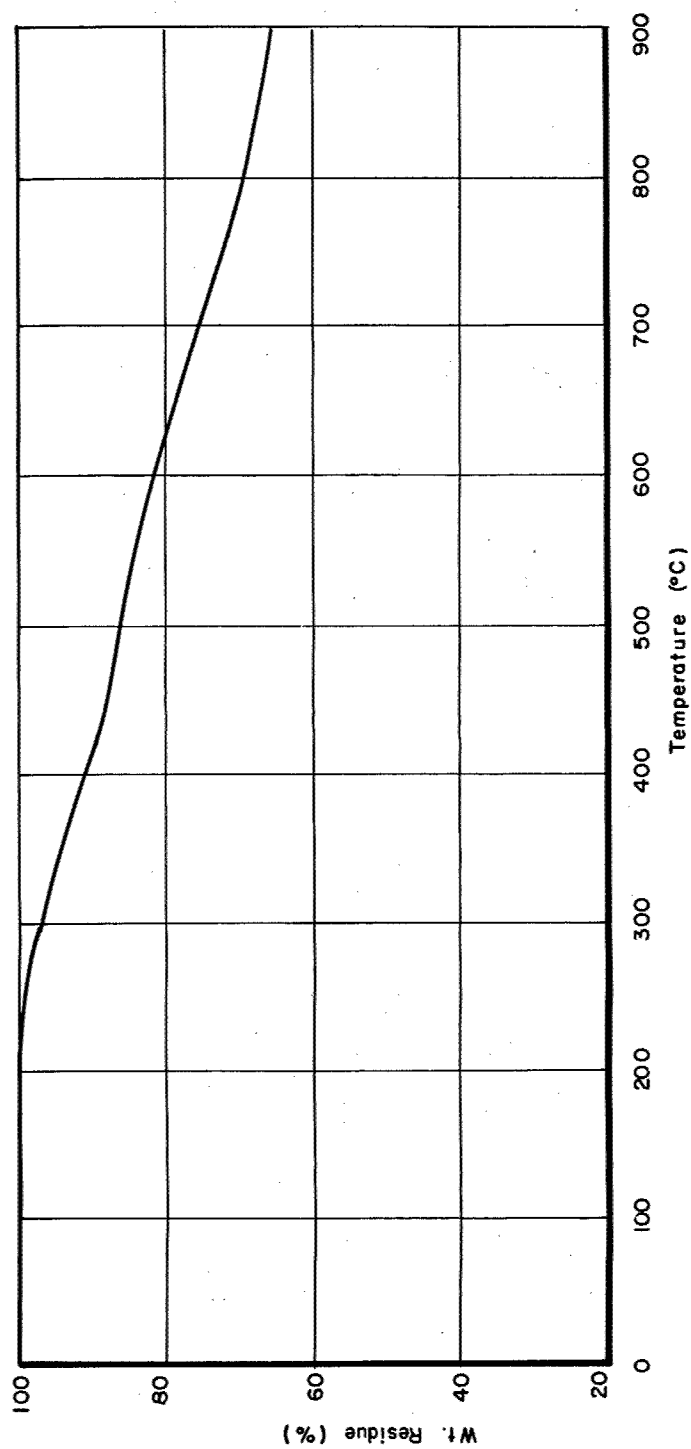


Figure 20 TGA Curve of the Insoluble Polymer  $(C_{17}H_{15}O_3N_3)_7$   
XVII, (from run [K])

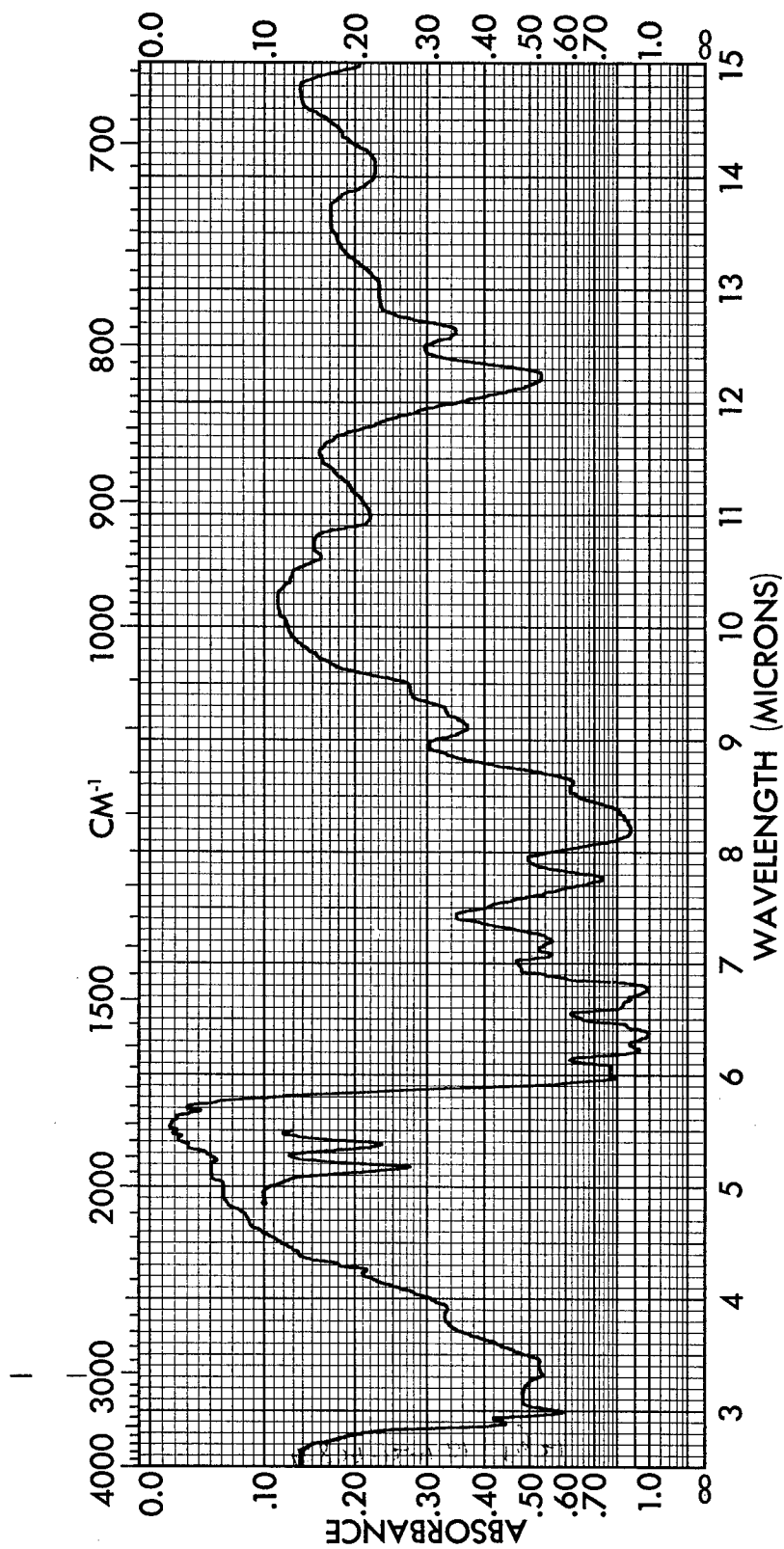


Figure 21 Infrared Spectrum of the Single Strand Polymer,  $(C_{14}H_{10}O_3N_2)_n$ , XIV, from Reaction of 6,6'-bis-[(2H), 3,1-benzoxazine-2,4, (1H)-dione] and Benzidine-3,3'-dicarboxylic Acid, XIII, in Dimethylformamide and Dilute Aqueous Sodium Hydroxide



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13. ABSTRACT <p>It has been found that a new compound, 6-dimethylamino-carbonyl-dibenzo-[b,f] [1,5]-diazocine-12, [11H]-one, is produced when either anthranilic acid or dibenzo-[b,f] [1,5]-diazocine-6,12, [5H, 11H]-dione is heated at 50 to 80°C in solution in dimethylformamide in the presence of a suspension of phosphorus pentoxide. A mechanism involving self condensation of anthranilic acid to dibenzo-[b,f] [1,5]-diazocine-6, 12 [5H, 11H]-dione followed by reaction with dimethylformamide is proposed.</p> <p>Polycondensation of ortho substituted diamino aromatic dicarboxylic acids such as 2,5-diaminoterephthalic acid, or benzidine-3,3'-dicarboxylic acid occurs in a similar fashion resulting in formation of double strand or ladder polymers of high molecular weight which can be extruded into fibers from concentrated sulfuric acid or from methane sulfonic acid. These new ladder polymers have a high degree of thermal stability and contain at least one dimethylaminocarbonyl group for each unit in the polymer chain. The polymers appear to be hygroscopic and easily absorb water to give a hydrated structure which contains about one molecule of water for each dimethylaminocarbonyl group. This absorbed water is removable by vacuum drying.</p>			

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